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VH

THE ASSAYER'S MANUAL.

AN ABRIDGED TREATISE

ON THE

DOCIMASTIC EXAMINATION OF ORES, AND FURNACE AND OTHER ARTIFICIAL PRODUCTS.

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BY

BRUNO KERL,

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TRANSLATED FROM THE GERMAN

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PREFACE TO THE AMERICAN EDITION.

In view of the well-known thoroughness and accuracy of Bruno Kerl's various metallurgical works, the preparation of the present edition of his abridged MANUAL OF ASSAYING has been undertaken with the conviction that it would be doing a real service to English speaking students and teachers of the subject. Though presented in very condensed form, every method of importance will be found to have received notice, and its practical value duly estimated at its proper worth.

The utility of the translation it is hoped will be found to be increased by the introduction of the English equivalents of the French metric weights and measures, wherever these occur throughout the work. In other respects the aim of the translator and reviser has been to preserve in its integrity the text of the original work.

W. H. W.

PHILADELPHIA, April 5, 1883.

AUTHOR'S PREFACE.

THE object of the "Assayer's Manual" is to give directions for executing docimastic tests of natural and artificial products by methods taken mostly from practice, and which are of interest especially to metallurgists, but also to other technologists. To those possessing some knowledge of chemical and docimastic manipulations, the aphoristic mode of expression I have chosen will be sufficiently clear to enable them to execute the tests without further instruction. Those less skilled are referred for details to my larger work on "Assaying," Leipzig, 1866. Copious bibliographical references are given in the foot-notes, which are calculated to help both the teacher and scholar.

As the assaying of iron has been thoroughly treated in my manual of "Assaying of Iron," Leipzig, 1875, the subject has been omitted in the present treatise.

B. KERL.

BERLIN, September, 1879.

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ASSAYING.

GENERAL DIVISION.

---

1. OBJECT OF THE ART OF ASSAYING.[1]

THE art of assaying (*docimacy*, from δοκιμαζειν, to test) is a branch of analytical chemistry. Its object is the quantitative determination, in the shortest possible time, of the products of mining and metallurgical operations, as well as the quantitative examination of many natural and artificial products derived from other sources, such as coins, fuels, etc. Formerly, in order to reach the result with the greatest expedition, the dry method (*dry assay*) was chosen for producing the chemical reaction; but, as this was frequently done at the expense of accuracy in the result of the assay, the *wet method* (wet assay, *gravimetric analysis*, *analysis by measure* or *volumetric analysis*, and *colorimetric analysis*) is also used in modern times. But it has by no means entirely displaced the dry method, for the latter is employed in all cases where results sufficiently accurate are more quickly reached, or where suitable, simple wet assay methods (as in assaying lead, cobalt, nickel, gold, and silver) cannot be substituted for it.

---

[1] **Kerl, Eisenprobirkunst, Leipzig, 1875. Balling, Probirkunde, Braunschweig, 1879. Mitchell, Manual of Practical Assaying, London, 1868 Ricketts, Notes on Assaying and Assay Schemes, New York, 1876.**

Sometimes a combination of both is employed (assays of lead, gold, etc.). Recently the method of *precipitating* metals *by electrolysis*[1] has been employed to great advantage (copper, nickel, cobalt).

Volumetric assays can mostly be performed in a shorter time, which is an important item where much assaying has to be done. The results they yield are either very accurate, or at least sufficiently exact[2] for metallurgico-technical purposes; they are less expensive, but require greater experience and more chemical knowledge on the part of the operator, and special apparatus of accurate construction. While by the dry method the metal assayed, or one of its alloys having a known composition, is weighed directly, in volumetric assays it is calculated from certain reactions of the reagents employed, and the result may possibly be vitiated on account of the presence of foreign substances, of whose presence there is not always an indication.

Colorimetric assays are chiefly employed for determining very small quantities of metals which either could not be detected by other methods, or, if so, then only by very tedious processes (copper, lead); but recently they have been developed so as to adapt them for substances rich in metal (copper).

The *blowpipe* is frequently used for a preliminary assay.[3]

---

[1] B. u. h. Ztg., 1869, p. 181 (Luckow); 1875, p. 155; 1877, p. 5 (Schweder). Grothe, polyt. Ztschr., 1877, p. 11 (Bertrand).

[2] B. u. h. Ztg., 1869, p. 330. (Compare gravimetric and volumetric assays of Cu, Fe, Zn, Sb.)

[3] Berzelius, Anwendung des Löthrohrs, Nürnberg, 1828. Scherer, Löthrohrbuch, Braunschweig, 1857. Birnbaum, Löthrohrbuch, Braunschweig, 1872. Simmler, Löthrohrchemie, Zürich, 1873. Hirschwald, Löthrohrta-

I. Mechanical Manipulations.

2. SAMPLING.

It is absolutely necessary that the small quantity of sample with which the assay is made, should represent the average composition of the ore-heap, etc., from which it is taken. The manner of taking samples varies according to the character of the substances to be assayed, viz.:—

A. Non-alloys (ores, matt, speiss, slag, etc.).

1. *Substances in fragments*, either homogeneous or heterogeneous in composition.

a. *Homogeneous fragments*, many iron ores, lead and copper ores, etc.

α. Samples from the heap.[1]—Pieces are taken at random (it is best to do so with bandaged eyes) with the hand or a shovel, from different places on the circumference of the heap, and also from the interior, after the upper layer which has been dried by the atmosphere has been removed. The collected lumps (about 100 kilogrammes, 220.54 lbs.; in Freiberg, for certain ores, one-tenth of the heap) are comminuted to pieces of the size of a bean, either by means of rollers or stamps, or with a sledge-hammer. A square or conical heap is then formed of the pieces, and this is divided into four parts. One of these is taken, the pieces forming it are still further comminuted, and then again formed into a heap, which is divided as before. The comminution and reduction are repeated several times, finally upon an iron plate

---

bellen, Leipzig, 1875. Landauer, Löthrohranalyse, Braunschweig, 1876. Kerl, Löthrohrprobirkunst, Clausthal, 1877. Landauer, systematischer Gang der Löthrohranalyse, Wiesbaden, 1878. Plattner-Richter, Probirkunst mit dem Löthrohr, 4 Aufl., Leipzig, 1878.

[1] B. u. h. Ztg., 1868, p. 26; 1872, p. 59.

provided with a rim (reducing-board), until at last from ½ to 1 kilogramme (1 to 2 lbs.) of the sample remains, in such comminuted form that it will pass through a sieve having 30 by 30 meshes to the square centimeter (about 75 meshes to the inch).

β. *Samples taken while the ore, etc., is being weighed.*—Pieces are taken at random from every lot weighed, and the collected pieces comminuted and reduced according to paragraph α (Upper Harz copper pyrites).

γ. *Samples by rasping.*—Fuels, etc., which cannot be pulverized are comminuted by a rasp, and a reduced sample made from this.

δ. *Slag samples.*—A piece of slag is taken every time the slag is tapped or run off, or a piece is broken off from every cone formed. The pieces of one charge are comminuted and reduced in the manner above stated.

b. *Heterogeneous fragments.*—(Gold and silver ores, many copper ores, coal with slate and pyrites, etc.)

α. *Sampling by the crossing method.*[1]—When the grains are too dissimilar and too coarse, the entire heap is broken up. The broken fragments (as large as a walnut for less valuable ores, and about the size of a hazelnut or bean for the more valuable) are passed through screens or cylindrical sieves. An oblong or square heap, 30 to 40 centimeters (about 12 to 15 inches) high is then formed. Ditches about 20 to 30 centimeters (about 8 to 12 inches) wide, and crossing each other, are dug out with a shovel, and the samples are then taken by digging them out from the top down to the bottom of the squares, which remain standing between the ditches. These samples are comminuted to the size of millet-seed, thoroughly mixed, and formed into a new rectangular heap, which is again crossed, and samples taken from it in the manner stated. This operation is repeated, finally by using the spoon, until the samples are reduced to a powder. (Method in the great ore markets of Swansea and Liverpool, for American silver ores in the Upper Harz and in Freiberg, etc.)

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[1] Preuss. Ztschr. xvii. 137 (Mansfeld); xviii. 223, 224 (Swansea).

β. Sampling by dropping the ore.[1] (Sturzprobe.)—The ore is dropped through a funnel standing over a pyramid of sheet iron, which is divided into four divisions by partitions projecting over the edge, into which the ore is distributed. The ore from one of the divisions is comminuted and dropped through a funnel into a similar but smaller pyramid. This operation is repeated, smaller pyramids being used every time, until a sufficiently reduced sample has been obtained (method in Chili and Colorado).

2. *Small ore and pulverized substances.*

a. Sampling while weighing.—The small ore must be carefully mixed, and, in case it should be rich, it is best to have it in such a condition that not over 15 per cent. of coarse material will remain behind in passing it through a sieve having 10 meshes to the square centimeter (25 meshes to the inch), but, otherwise, it may be coarser. It is generally weighed in quantities of 50 to 100 kilogrammes (say 100 to 200 lbs.). Three spoonfuls are taken from different places of every lot weighed, and placed in wooden troughs standing near the scale. All the samples taken from one lot are mixed together and a heap is formed from them. This is reduced by quartering, or by the crossing method.[2]

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[1] Preuss. Ztschr. xxiv. 49. B. u. h. Ztg. 1872, p. 232 (Chili). Ann. d. Mines, 1878, XIII. 606 (Colorado).

[2] Kerl, Oberharzer Hüttenprocesse, 1860, p. 195.

Samples of goldsmiths' *sweepings* (scrapings, fragments of crucibles, rags, etc.) are taken by incinerating the entire mass in order to destroy organic matter. The mass is then comminuted by stamping or trituration, and passing it through a sieve having meshes the size of a grain of sand (less than 1 millimeter, 0.039 inch). The iron in the coarse mass remaining in the sieve is extracted by using a magnet, and the residue fused with soda and borax, cast into a bar, weighed, and sampled by chipping from top and bottom. The portion that has passed through the sieve, freed from iron with the magnet, is then weighed, sampled from every weighing, then united, quartered, and triturated until everything passes through a very fine sieve. It is then assayed, and the yield of metal obtained from both coarse and fine material is calculated.

b. Sampling before weighing.—This is done by passing with a hollow sheet-iron cylinder in several places through the heap down to the bottom. The lower end of the cylinder is provided with a valve which when closed retains the charge, and with a handle. The samples are then mixed and reduced as above described (Freiberg).

In some of the German smelting works, the ore,[1] when it is bought, is weighed

to within 10 lbs. (5 kilog.; 11 lbs.) when it contains up to 0.5 per cent. Ag, or 0.01 per cent. Au.
" 1 lb. when it contains over 0.5–5 per cent. Ag, or 0.0105–0.1 per cent. Au.
" 0.1 lb. when it contains over 5–50 per cent. Ag, or 0.1005–1 per cent. Au.
" 0.02 lb. if it contains more.
" 10 lbs. if the ores contain no gold or silver.

3. *Substances in a state of fusion.*—An average sample may be obtained in the following manner: A dry tapping-bar, previously heated, is held in the fluid mass (slag,

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[1] Bezahlungstarife für den Einkauf von fremden Erzen u. Gekrätzen auf den fiscalischen Hüttenwerken bei Freiberg. Clausthal, 1870. Oestr. Ztschr. 1869, No. 44. Engl. Standard f. Zinnerze, B. u. h. Ztg. 1862, p. 261; f. Kupfererze, 1862, p. 316. Spanische Tarife, B. u. h. Ztg. 1868, p. 26. Tarnowitzer Erztaxe in Preuss. Ztschr. xiv. 217.

etc.). When the bar has become cold, the adhering mass is broken off, comminuted, and then mixed and reduced. In this operation, however, the iron must not decompose the fused material (a possible separation of lead may occur, for example, from lead-matt and lead speiss).

B. Alloys.—These are homogeneous when in a fluid state, especially after they have been stirred. But when solidified, they show a different composition in different places (edge, centre, top, bottom).[1] In sampling, this must be taken into consideration.

1. *Sampling by cutting.*—The sample (2.5 grammes (38.59 grains) from every ingot of silver, 1.5 grammes (23.15 grains) from those of gold) is cut from the upper and lower sides on opposite ends of the ingot by means of a hollow chisel and hammer. (In England and the United States, the opposite edges are chipped off.) The samples are hammered or rolled out, the resulting sheets cut into shreds, and each sample is assayed by itself (0.5 to 1 gramme, 7.71 to 15.43 grains, of each is weighed off for the purpose). The yield is calculated, and either the average is given (gold assays), or the lowest yield (sometimes in silver assays). This method is best adapted for alloys of tolerably uniform composition, but is also employed for those showing a considerable difference in the lower and upper sampling.

For instance, the lower sample from refined Upper Harz silver is from $\frac{3}{1000}$ to $\frac{4}{1000}$ richer than the upper, the percentage of gold increasing towards the bottom. The centre, as a rule, contains more silver than the edge. In the "*five-mark piece*" the centre is $\frac{2}{1000}$ richer than the edge, and the same is the case with the "*thaler*," as they are stamped from a bar poorer on the edge than in the centre. For this reason, when taking samples from such coins, it is best to cut out a quadrant, cut off the corners, and assay them. In this way the assay samples represent the composition of both periphery and centre of the bar from which the coins have been stamped. Fewer differences occur in gold than in silver coins.

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[1] Kerl, Grundr. d. allgemeinen Hüttenkunde, 2 Aufl., 1879, p. 15. Dingler, cciii. 106; ccxv. 431. Ber. d. deutsch. chem. Ges. 1874, p. 1548, B. u. h. Ztg. 1874, p. 63; 1875, p. 251.

2. *Sampling by boring.*[1]—This is done by boring through the edge and centre of the ingot. By this means a sample is obtained from the centre of the ingot, which is not the case in chipping a sample, but the ingot is made unsightly. It is very difficult to mix the borings uniformly, and it is therefore better to fuse them under a covering of charcoal powder. It is best to use a mechanical contrivance for boring through thick pieces. This consists of a lever weighted at one end, and a drill, operated by the hand in the centre.

3. *Sampling by dipping.*—This is obtained in the same manner as mentioned on p. 22, for instance, from refined copper. Another method of taking samples is, by dipping the curved, bright end of a pair of pincers, or of an iron rod, into the metal bath. When the pincers or iron rod has become cold, the crust adhering to the end is broken off. A sample is generally taken from the surface of silver while it is being refined, and one from the under side of the congealed refined silver.

4. *Sampling by granulation.*—This sample indicates in the most reliable manner the average value of the metal. It is obtained in the following manner: the bars of precious alloys are smelted in a black-lead crucible. The mass, while in fusion, is stirred with a rod of iron or clay, and a sample is scooped up with a small ladle from the bottom of the crucible. It is then poured in a thin stream into a copper vessel filled with warm water, to

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[1] Mitchell, Prac. Assaying, 1868, p. 565.

which a gentle rotary motion is given by means of a broom; or the sample is directly poured through a birch broom. The resulting granulated metal is then carefully dried. Alloys of base metal (as granulated lead[1]) are fused under coal-dust and then directly poured upon an iron plate.

The following samples are taken for producing coins: *ingot sample* from the metals to be alloyed; *granulated* or *crucible sample* from the fused alloys; *stock sample* from sectors of the finished coins; and a *sample* from defective coins which have been thrown out and fused together, for instance inside of four weeks.

3. PREPARATION OF THE SAMPLE.

Alloys are prepared by rolling out and cutting up the resulting sheets; or the granulated metal is used without further preparation. The following operations may be required for non-alloys.

1. *Determination of moisture.*—The sample is divided, by weighing with reduced weights, into as many centners or kilogrammes as are actually contained in the lot (for instance, in Freiberg, 1 centner weight =75 grammes or 1157.87 grains). The weighed portion is heated in an iron or copper pan or directly in the removable scale-pan of the balance, by holding it over a heated stove or a brazier of charcoal, and constantly stirring it until a cold plate of glass or slate, when held over it, shows no deposition of moisture, and two successive weighings agree. The heating should be carefully conducted, so that, with sulphur compounds for example, no odor of sulphurous acid shall be developed, and, with organic substances, no carbonization shall take place (this may be guarded

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[1] B. u. h. Ztg., 1869, p. 278 (Brixlegg).

against by holding a piece of paper in the mass). Water-baths are used for drying the sample at 100° C. (212° F.). These are copper boxes, with double walls, the intermediate space (Fig. 1) containing water; or, they consist of hemispherical copper or enamelled iron vessels, placed one within the other, leaving an intermediate space for water; or of two cylinders, one placed within the other (*Scheibler's*[1] steam apparatus). Where a determinate temperature, high or moderate, is required, it is best to use *Fresenius' drying disk* of cast iron, which is heated from below (Fig. 2). It is 25 centimeters (9.84 inches) in diameter, and 4 centimeters (1.57 inches) thick; *b* is the handle, 36 centimeters (14.17 inches) high; *c* are small brass dishes with numbered handles fitting into suitable recesses; *d*, a case filled with copper-filings for

Fig. 1.

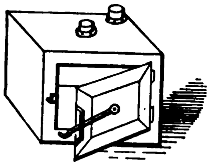
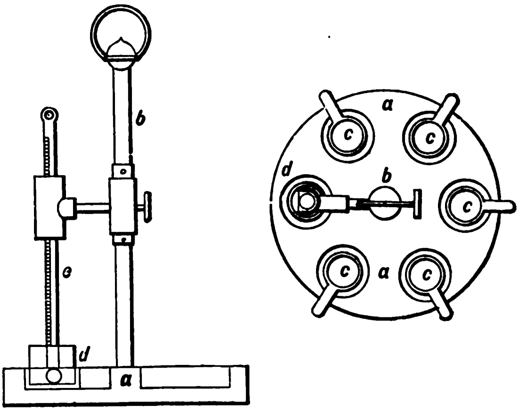


Fig. 2.



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[1] Dingler, ccxxiii. 312. Muspratt's Chemie, v. 1635.

the reception of the thermometer *e*. Besides these, *air-baths*,[1] commonly called thermostats, are also used.

2. *Pulverizing the desiccated mass.*—This should be done carefully, to avoid loss of dust, either in a covered mortar, or on a flat disk of cast iron.

3. *Sifting.*—Brass wire sieves are generally used in preference to hair sieves. For less valuable ores the sieves have from 14 to 20 meshes to the square centimeter (about 35–50 to the inch), and more valuable ores from 28 to 32 meshes to the square centimeter (from 70–80 to the inch). Brittle substances will pass through the sieves without difficulty, but those with malleable admixtures will leave a flattened residue in the sieve; as, for example, ores carrying native silver and copper, silver glance, granules of lead in slag and thin matt, sweepings containing gold and silver (p. 22), etc. In case *hard* gangue (quartz) is to be sifted, the fine mass which has passed through the sieve is several times rubbed together with the coarse residue remaining upon the sieve, until everything has passed through it. The residue of *soft* gangue is weighed and at once assayed by itself, and the fine siftings separately also, after they have been mixed upon glazed paper and passed several times through a coarse sieve. The entire yield is then calculated by adding the product of both together. The material ready for assaying is packed in wooden boxes, glass bottles, or small linen bags. Dishes of ordinary potter's clay (Mehlscherben) may serve for the reception of the stamped ore and lots of samples while they are weighed out for assaying; they have an outer diameter of from 80 to 100 millimeters (3.14 to 3.93 inches) on the bottom, 100 to 200

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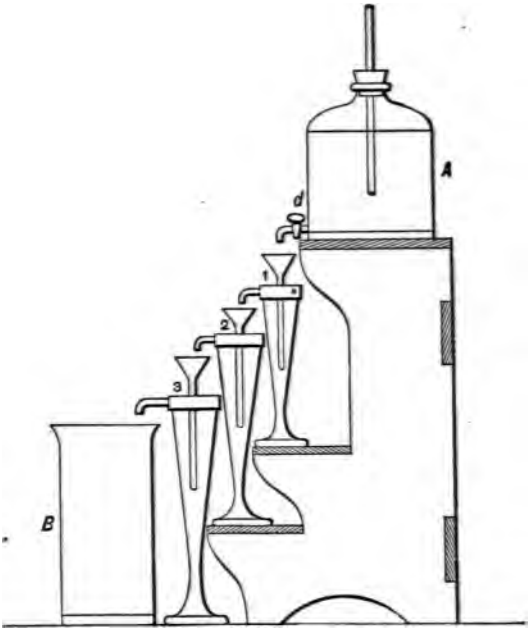
[1] Bunsen's Luftbad mit Temperaturregulator in Kerl's Grundr. der Eisenprobirkunst, 1875, p. 3. Raulin's Wärmeregulator in Dingler, ccxxvii. 263.

millimeters (3.93 to 7.87 inches) on the top, and are from 40 to 45 millimeters (1.57 to 1.77 inches) high (Hungary).

4. *Washing.*—This is done to separate specifically heavier substances from lighter ones (roasted tin ore, gold gravel, etc.), or to obtain a uniform grain (smalt assays). The mass, comminuted as fine as possible, is placed in a beaker glass and water poured upon it. It is then thoroughly stirred up, when it is allowed to settle, and the turbid liquid poured off; or it is washed in Schulze's washing apparatus (Fig. 3) by allowing water to flow from

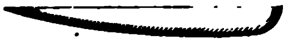
Fig. 3.



a *Mariotte's* bottle, *A*, through *d*, upon the mass contained in the glass 1; the different sizes of grain will settle in the glasses 2 and 3, the finest grains in the beaker-glass *B*. Another mode of washing the substances is by using a wooden vanning trough (Figs. 4 and 5), from 420 to 470 millimeters (16.53 to 18.47 inches) long, 160 to 210 millimeters (6.29 to 8.26 inches) wide,

Fig. 4.

Fig. 5.



and 35 to 40 millimeters (1.37 to 1.57 inches) deep; or they are washed upon a shovel 400 millimeters (15.74 inches) long, and of the same width (Cornish test of tin ore). The washed mass should be occasionally examined with a magnifying glass or blowpipe as to its physical characteristics (for instance, silver ore for the presence of metallic sulphides, antimony and arsenic, in order to regulate the addition of lead before assaying).

4. WEIGHING AND MEASURING.

Before every weighing [illegible] as to its equilibrium. [illegible] should be cold, and must [illegible] scale-pan, but upon [illegible] etc.; hygroscopic [illegible] and beam should [illegible] [illegible] before a weight [illegible] The weights must [illegible] systematically, [illegible] The highest [illegible] the next lower, [illegible] [illegible] [illegible] the correction [illegible] of the balance [illegible] correct weighing may be obtained by placing the substance to be weighed in one pan, and in the other pan, any convenient material as a make-weight, such as tinfoil, shot, granules of lead, etc., until equilibrium is established. The balance is then raised, the weighed substance is removed from the pan, and sufficient weights to counterpoise the balance are put in its place. The sum of these weights will give the correct weight of the sample.

1. *Weighing: a. A pulverulent sample.*—The dried sample is poured upon glazed paper and spread out in spirals with the spatula. It is then drawn together towards the centre by radial bands. Some of it is now taken with the spatula from the bottom to the top of the heap, the weights are placed upon the left pan of the balance, and the sample is continuously poured into a counterpoised saucer or watch-glass placed upon the other pan, by gently tapping on the handle of the spoon, until equilibrium has been established. In case too much has been poured in, some of it is removed, but the balance, while this is done, must be arrested. Large quantities are weighed upon a *watch-crystal* counterpoised by granules of lead or shot. Hygroscopic substances are conveniently weighed by filling a *stoppered glass tube*, 12 to 14 centimeters (4.72 to 5.51 inches) long, and 8 to 10 millimeters (0.31 to 0.39 inch) wide, with them, noting the weight, and, after pouring out the requisite amount of sample, again weighing the tube; the difference between the two weighings will give the weight of the quantity abstracted.

b. Alloys.—They are converted either into granulated form or into small strips or splinters. These are collected in a glass or copper saucer and placed by means of the forceps in the right pan of the balance while the weights are placed in the left.

c. Fluxes.—In weighing these, very great accuracy is not of so much importance. They are placed either directly upon the pan of the balance, provided it is not attacked by them, or otherwise upon a tared watch-crystal.

2. *Weighing the button.*—The button is taken hold of with the forceps and placed upon the left pan of the balance, and the weights are then put upon the right; but, as has been stated, the balance must always be arrested before the weights are put on or removed.

3. *Measuring of fluxes.*—Granulated lead (test lead) free from silver is measured with large, gauged, iron spoons numbered on the handles, or with a glass tube, one end of which is closed with a stopper, while in the other is a wooden cylinder provided with a scale.

5. MANNER OF CHARGING THE SAMPLE.

The sample is poured either directly into the crucible without any fluxes (as in roasting), or the fluxes are added in such a manner that—

1. The sample lies on the bottom of the crucible, and the fluxes are placed upon it in consecutive order without stirring the mass up. When this is done, the mass will not puff up as easily when it is heated (charges with carbonaceous mixtures, for instance, assay of lead with carbonate of potassa, flour and iron).

2. The sample is added to the fluxes already in the crucible, in cases where the puffing up of the charge on heating is not feared, and is intimately mixed together (for instance, assay of lead with potassium carbonate).

3. The sample is mixed with the fluxes before it is placed in the crucible. The mixing is done in a mixing-scoop of copper (Fig. 6) by means of a spatula. The

scoop is about 140 millimeters (5.51 inches) long and 40 millimeters (1.57 inches) wide.

Fig. 6.

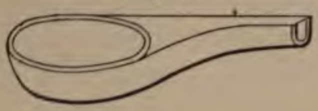
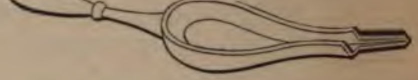


Fig. 6a.



The mixture is poured into the crucible through the spout of the scoop, about 20 millimeters (0.78 inch wide), a brush being used to brush out the last traces of the mixture; or, in case a very vigorous chemical reaction is desired, the sample and fluxes are first intimately rubbed together in a mortar of stone (porcelain, serpentine, agate), or of metal (steel, cast iron, brass). Open mixing scoops of copper provided with a handle (Fig. 6*a*) are used for mixing the charge, or for receiving, in consecutive order, the substances constituting it, or for pouring them into the glowing crucible standing in the heated furnace (assays of lead, English assay of copper).

II. Chemical Operations.

6. CLASSIFICATION.

These operations are divided into those by the *dry* and those by the *wet method*, and are either preliminary (roasting, etc.), or capital operations (smelting, etc.).

7. WORKING BY THE DRY METHOD.

These operations are carried on, either below the fusing point (*ignition*, *carbonizing*, *calcining*, *roasting*), with or without admittance of air; or at a fusing heat (smelting); or volatile substances are to be expelled by heat and their vapors condensed to the liquid state (*distillation*), or to the solid state (*sublimation*).

1. *Ignition, carbonizing, calcining.*[1]—Heating without fusing—

a. In a *neutral atmosphere*, to drive out volatile substances (for instance, water and carbonic acid from iron ores), or to change their molecular condition (for instance, annealing gold and silver alloys before rolling them out, etc.).

b. *With exclusion of air* in covered pots or crucibles, to decompose metallic sulphides and arsenides (iron and arsenical pyrites in the dry assay of blende), to effect reduction (ignition of tin ore with charcoal), or to arsenize or dearsenize the substances (assay of nickel and cobalt).

c. *With admission of air* in roasting dishes (determination of ash in fuel, combustion of bitumen in copper schist and black-band iron ore, oxidation of cement copper, etc.).

d. *With reagents for decomposing* substances insoluble in acids (for instance, silicates with four times their weight of a mixture of 13 parts of potassium carbonate and 10 parts of anhydrous sodium carbonate in a platinum crucible).

2. *Roasting.*—Metallic sulphides, arsenides, and antimonides are heated in presence of air to a temperature insufficient for fusion, but which permits of their oxidation; metallic oxides are, therefore, produced, while sulphurous, arsenious, and (sometimes) antimonious acids are volatilized.

The process is as follows: The powdered sample is spread out in a shallow, smooth roasting dish. This is about 50 to 52 millimeters (1.96 to 2.04 inches) wide in the clear, and 8 to 10 millimeters (0.31 to 0.39 inch) deep, made of not too refractory clay, and has rather thin sides. It is lined with reddle, chalk, or oxide of iron, and, if necessary, in order to increase the surface, the lined sides are marked with a spatula in such a manner that radial furrows, running from the centre towards the edges, are formed. It is then placed in the muffle of a muffle-furnace (Fig. 25) and heated at a gradually increasing temperature until it glows; the heating must be the more gradual the more fusible the sample. (Antimonial and arsenical metals are more easily fused than metallic sulphides, antimony glance, lead sulphate, and "fahlerz" containing mercury). The mouth of the muffle is left open, with the exception of a low layer of pieces of wood charcoal touching each other, and continued in a forward direction. These pieces in a glowing state heat the oxidizing air current. The roasting dish must occasionally be turned around during the operation. It is taken from the muffle when the mass has ceased to burn, and oxidation is complete. This is indicated by the heated mass ceasing to fume and no longer emitting odors of sulphurous or arsenious acid, and by the metallic lustre having been replaced by an earthy appearance. If this should not be the case, the roasting dish must be placed back into the muffle until these signs make their appearance. The now roasted sample may be somewhat sintered together. It is then rubbed with the iron knob, *b*, of a wooden-handled spatula, after being loosened from the edges of the roasting dish with the knife's edge, *a*, of the rod. This tool (Fig. 8) is about 195 millimeters (7.67 inches) long, and consists of the iron head *b*, about 16 millimeters (0.63 inch) diam., and

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[1] Gaslampen in Dingler, ccxxiv. 617; ccxxv. 83 (Müncke). Fresenius' Ztschr. 1879, p. 257 (Ebell). Bunsenbrenner von Glas in Dingler, ccxxvii 85, 398.

Fig. 7.

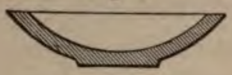

Fig. 8.

the steel knife-blade *a*, set in a wooden handle. The roasting is repeated once or several times, but the mass must be rubbed up previous to each roasting. It is then mixed with 1 or 2 volumes of powdered wood charcoal, or 20 to 25 per cent. of graphite, and the roasting dish with its contents is again placed in the muffle and brought to a glow. By this process the sulphates, antimoniates, and arseniates formed during the oxidizing period are reduced to metallic sulphides, antimonides, and arsenides, while the volatile products of oxidation escape (*reducing roasting*). These compounds when all the carbon has been consumed (which may be readily recognized by the manner of glowing) will be again converted into oxides; sulphurous, arsenious, and antimonious acids being evolved in the operation. But new sulphates, antimoniates, and arseniates will constantly be formed, and these, if the sample is to be roasted as completely as possible (for instance, copper ores, but lead ores in a less degree), can only be removed by repeating the rubbing up of the assay sample twice or three times, mixing it with charcoal powder, and glowing until the coal is *completely* consumed, although even after this small quantities of sulphates will nevertheless remain. When the roasted sample has become sufficiently cold, it is placed in an iron mortar and mixed with 20 to 50 per cent. of ammonium carbonate. A small conical heap of the mixture is formed in the roasting dish, this is covered with an empty roasting dish and quickly ignited until the odor of ammonia can no longer be detected. When this is the case, the last traces of sulphuric acid in the roasted sample will have been volatilized in the form of ammonium sulphate. (Lead and bismuth sulphates are only incompletely decomposed by ammonium carbonate.) The roasting dish is now taken from the muffle and allowed to cool off. The sample is then placed in a mortar and rubbed up.

Modifications.—When the ores are refractory (for instance, copper pyrites), powdered charcoal or graphite is added to the sample before roasting, in order to shorten the time required for the operation. Very fusible substances which evolve vapors (such as "*fahlerz*" containing mercury) must be heated very gradually. To diminish the loss of metal (for instance, of silver and gold) the temperature must not be raised higher than is absolutely necessary. The loss from this cause is greatest with ores containing antimony, arsenic, zinc, etc.

3. *Fusion.*—The sample is brought into a liquid state, either by itself, or with fluxes. During this process the resulting products (metal button or regulus, speiss, matt, slags) arrange themselves in layers according to their specific gravities, and are separated from each other, either by breaking to pieces the clay assay-vessels in which they have been fused, after they have become cold, or they are poured out while still in a fluid state, into iron or bronze moulds, where the separation then takes place. Sometimes the fluid, oxidized substances are absorbed by the porous sides of the assay-vessel, leaving the metal button behind (cupellation of lead, and refining copper on the cupel). The following distinctions are made according to the object of the fusion:—

a. Oxidizing fusion.—In this process the following may serve as oxidizing agents: the oxygen of the air, demanding open vessels for the operation (cupels, calcining and roasting dishes), which must be heated in the muffle-furnace (for instance, cupellation of lead, refining copper, assay of cobalt and nickel); or fluxes yielding oxygen, and then open or covered assay-vessels (pots, crucibles), and muffle, wind, and blast furnaces may be used (saltpetre in the Cornish assay of copper and in the assay of chromium, lead oxide in the assays of fuel, silver and gold); or both at the same time (refining of black copper). The resulting oxides are more frequently slagged off by themselves or by solvent agents added as a flux (borax, glass, etc.), than absorbed by the porous vessel used for fusing (cupels).

b. Reducing fusion.—This operation is seldom executed by itself with reducing agents (coal, flour, colophony, potassium cyanide), but generally in connection with fluxes (potassium or sodium carbonate), in order to allow of a better collection of the particles of metal (as from litharge, white-lead ore); or in connection with reducing, fluxing, and solvent agents (borax, glass, phosphorus salt). A definite *low* temperature must then be used to reduce one metallic oxide, while the metallic oxides more difficultly reducible, are slagged off with the earths which may be present (assays of lead, copper, and tin ores). Muffle, wind, and blast furnaces are used. The vessels used for this process (crucibles, pots) should be roomy, as the mass puffs up. This is caused by the formation of carbonic oxide which ignites above the vessels. This phenomenon is called "*flaming*," the end of the operation being generally indicated by its cessation.

c. Purifying fusion.—This is more frequently used in connection with oxidizing fusion (p. 36) and reducing fusion (p. 37) than by itself (assay of smalt, assay of thin matt).

d. Precipitating fusion.—By this process metallic sulphides (in assays of lead, bismuth, and antimony) or arsenical metals (in the assay of lead ores and nickel and cobalt ores containing bismuth) are decomposed by iron. The desulphuration of the metals is promoted by suitable fluxes (potassium or sodium carbonate, black flux), or the slagging off of earthy and other admixtures is effected (borax, glass, alkalies).

e. Mixing fusion, to prepare alloys by fusing different metals together (gold and silver in quartation).

f. Remelting, in order to produce the sample in another form (as, for instance, by granulation, p. 24).

g. Liquating fusion (*liquation*).—Liquation of easily fusible substances from more refractory substances (assay of antimony glance).

4. *Sublimation and distillation.*—The sample is placed, either by itself or with fluxes, in crucibles, tubes, or retorts, and heated until the substances volatilize, and the vapors are then condensed as sublimates (flaky arsenic, flowers of sulphur, realgar), or as distillates (mercury, zinc) in suitable condensers.

8. OPERATIONS BY THE WET METHOD.

These may be—

1. *Assays by gravimetric analysis.*[1]

a. The sample is dissolved in acids, in a porcelain dish covered with a watch-crystal. Or a bellied flask is used for the purpose (Fig. 9). This either stands upright and is provided with a funnel, or is placed in a slanting position to prevent the liquid, in case it effervesces, from being thrown out of the mouth of the flask. The vessel may be heated on

Fig. 9.

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[1] Rammelsberg, quant. Analyse, Berlin, 1863. Wöhler, Mineralanalyse, Göttingen, 1861. Sonnenschein, quant. Analyse, Berlin, 1864. Rose-Finkener, Mineralchemie, Leipzig, 1865. Fresenius' quant. Analyse, 6 Aufl. 1871. Classen, quant. Analyse, Stuttgart, 1857. Menschutkin, analyt. Chemie, Leipzig, 1878. Bolley, techn.-chem. Unters., Leipzig, 1879. Muspratt's techn. Chemie, 3 Aufl.

a sand-bath, or upon a wire gauze over a lamp, until the solution is complete, or a residue showing no trace of ore, etc. remains.

The following method is used for metallic sulphides, which, when they are dissolved with acids, separate sulphur which incloses some of the ore. The solution is evaporated to dryness in a porcelain evaporating dish. The dry mass is heated over a lamp until the sulphur is burned. The residue is digested with a small quantity of acid, water is added to this, and the fluid then partly filtered; but in doing this great care must be observed. The residue is again treated with acid, evaporated to dryness, the sulphur burned, etc. If it is necessary to exclude the air, the apparatus represented in Fig. 10 is used. It consists of a flask, *a*, with a rubber cork, *b*, and provided with a rubber tube, *c d*, having a slit at *f*, and closed at *e* by a small glass rod.

Fig. 10.

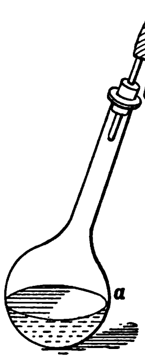
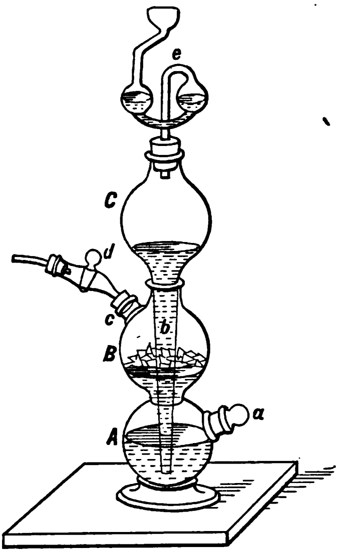


Fig. 11.



b. Evaporation of the solution in a glass flask (Swedish assay of copper, assay of lead sulphate), or in a covered porcelain dish by heating it in the sand-bath, over a lamp, or on the water-bath.

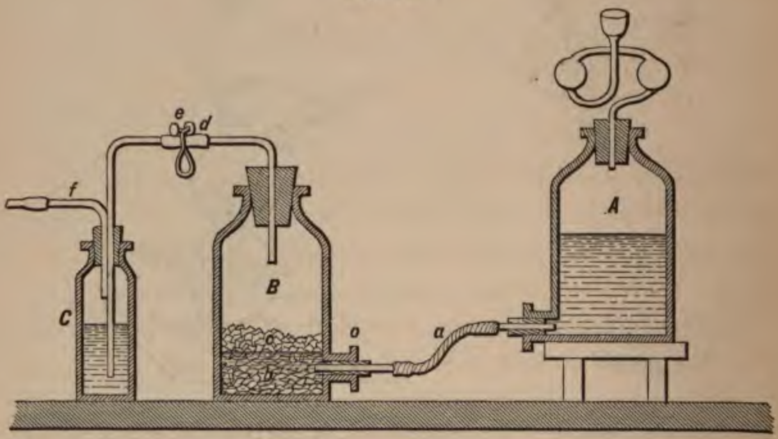
c. Precipitation of the filtered or unfiltered solution; or where a mass evaporated to dryness is to be treated, it is moistened with a little acid, allowed to stand for a few minutes, and then boiled with the addition of a small quantity of water. It is then filtered, etc.

Kipp's apparatus (Fig 11) is well adapted for precipitation with sulphuretted hydrogen.

C, a glass bulb, receives the diluted sulphuric acid from the funnel tube *e*; the acid enters the glass bulb *A* through the tube *b*. It rises in this and comes in contact with ferrous sulphide or calcium monosulphide contained in the bulb *B*, and the gas generated escapes by the tubulure *c* through the lateral tube controlled by the cock *d*; the tubulure *c* also serves for filling the bulb with ferrous sulphide; *a* is the tubulure for emptying *A*.

Debray's apparatus (Fig. 12) is arranged in the following manner: *A* is the vessel for the diluted sulphuric acid, provided with a safety tube and a rubber tube *a*. *B* is a vessel containing a layer of glass splinters, piled up so high that the ferrous sulphide, lying upon it, is above the opening *o*. *d* is a glass tube provided with a clip (compression stop-cock) *e*; *C* is a wash-bottle, *f* the pipe for conducting away the gas. By opening the cock *e* the acid flows from *A* into *B*, and sulphuretted hydrogen is disengaged. By closing the cock the fluid is

Fig. 12.



forced back from *B* into *A*; the pressure of the gas may be increased by placing *A* higher up. Instead of sulphuretted hydrogen, sodium hyposulphite may be used as a precipitating agent.

d. Filtration.—A funnel, the sides of which have a slope of 60°, is generally used for this process; a filter of paper is folded into it, and, if necessary, covered with a watch-glass. If the filtration is to be done quickly, the filter is connected with an air-pump,[1] or compressed air is used.[2] Fig. 13 shows a *filtering apparatus* connected at *a* with a water air-pump. The mouth of the flask is furnished with a rubber stopper perforated for the reception of the funnel. The dotted lines below this represent a perforated test-tube, through which the liquid is drawn into the flask. The precipitate on the filter is washed[3] by means of a wash-bottle (Fig. 14).

Fig. 13.

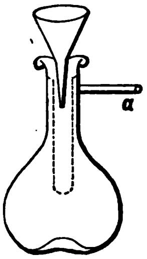
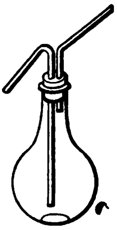


Fig. 14.



e. Decantation.—When a precipitate thoroughly settles, the clear supernatant liquid may be poured off. The precipitate is then repeatedly washed with water and decanted. To dry the precipitate, the contents of the flask (a glass

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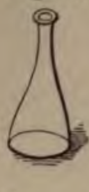
[1] Fresenius, quant. Analyse, 1871, p. 97. Fresenius' Ztschr. f. analyt. Chem. ii. 359; iv. 46; 1875, p. 308.

[2] Fresenius' Ztschr. xvi. 92. Dingler, ccxxv. 81, 105.

[3] Bunsen's Auswaschen der Niederschläge in Fresenius' Ztschr. viii. 174.

Fig. 15.



vessel (Fig. 15) with straight sides), is washed into a crucible or evaporating dish, with as little wash-water as possible (precipitated copper and gold, tin stone purified by boiling with acid); or the precipitate is filtered off, and, if necessary, also the sediment remaining, after the water used for decanting has been poured off.

f. Drying precipitates.[1]—The filter,[2] without being taken from the funnel, is covered with paper, to protect it against dust, etc., and dried in an air-bath, or a water-bath. Or, it is removed from the funnel, folded up and dried first between blotting paper, and then in a covered roasting-dish, in the muffle-furnace (assay of lead with sulphuric acid).

g. Igniting precipitates.[3]—If the substance is not to be weighed upon the dried filter, it is highly heated with the filter in the roasting-dish after the lid has been removed. Or, the precipitate is carefully detached from the filter; the latter is folded up, wrapped around with platinum wire, and is then burned over a flame or directly upon the cover of a platinum crucible, or in a roasting-dish. The residue, together with the ashes of the filter, is placed on a roasting-dish and ignited in a muffle-furnace, or in a platinum or porcelain crucible over a Bunsen burner, an ordinary spirit-lamp (Fig. 16), or a blast-lamp. The latter is represented by Fig. 17. *s s* is a partition separating the air-space *u*, from the gas-space *g*; *e* are five double-tube gas-burners, the inner tubes of

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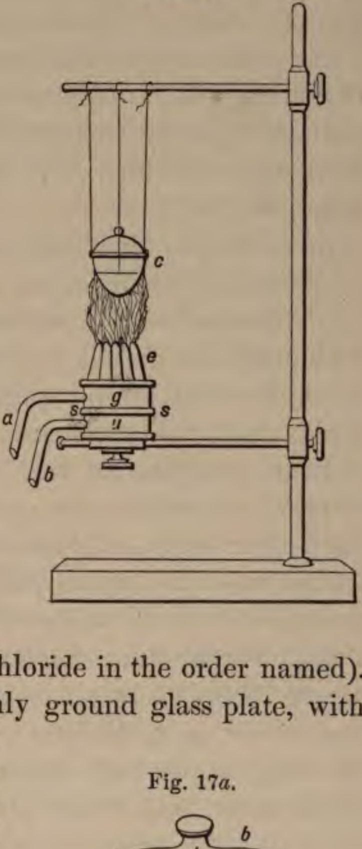
[1] Mürrle, of Pforzheim, furnishes distilling apparatus and sand-bath very suitably combined, with steam and air drying closets (these are in use in the Berlin School of Mines). Bestimmung der Niederschläge ohne Filtriren, Auswaschen und Trocknen in Fresenius' Ztschr. 1877, 157; 1879, p. 14.

[2] Filtrirpapiere in Fresenius' Ztschr. xvi. 59; xviii. 246, 260.

[3] Fresenius' Ztschr. 1875, p. 328.

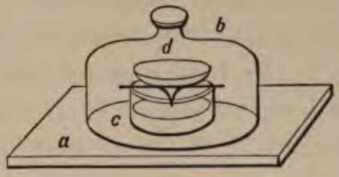
Fig. 16.

Fig. 17.



which reach into *u*, while the outer tubes only reach to *g*; *a* is the pipe for conducting illuminating gas; *b* for the air-blast; *c* the crucible. If necessary the crucible is allowed to become cold by placing it in the desiccator (Fig. 17*a*), in which are fragments of caustic alkali, calcium chloride, or sulphuric acid (caustic soda attracts water with the greatest avidity, next follow caustic potassa and calcium chloride in the order named). In the figure, *a* is a smoothly ground glass plate, with which *b*, a bell-glass, makes an air-tight joint; *c*, cup with concentrated sulphuric acid, and *d*, the dish or crucible with the precipitate to be dried, resting upon it.

Fig. 17*a*.



2. *Assays by volumetric analysis*[1] (p. 17).—By this

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[1] Schwarz, Maassanalyse, Braunschweig, 1853 und 1873. Schwertfeger, Maassanalyse, Regensburg, 1857. Gräger, Maassanalyse, Weimar, 1866. Fleischer, Maassanalyse, Leipzig, 1867. Fleischer, Titrirmethode, Leipzig,

method, the quantity of a substance in solution is determined from the volume of a solution of another body, which produces with the first a definite reaction, and the strength of which per unit of volume of its solution is known (called a standard solution or normal solution). The result is then found by calculation from the quantity of normal solution employed. The *final reaction*, which can sometimes be recognized only by a change occurring in another substance, especially added to the fluid (*indicator*), may be known—

a. In saturating a base or an acid with the normal solution (analysis by saturation), by a *change of color*, or by *decolorization* of a colored solution (assay of copper with potassium cyanide), or by an indicator such as litmus, which is added for the purpose, as in the estimation of acids or alkaline carbonates.

b. In precipitating the body to be determined, with a standard solution, *when precipitation ceases* (Gay Lussac's silver assay), or by some *change in an added indicator* (Schaffner's zinc assay; Pelouze's copper assay); and frequently also by the *drop-test*, that is, a drop of the assay fluid and of the indicating fluid are brought in contact upon a porcelain plate by means of a glass rod, or alongside of each other upon filtering paper, in such a manner that the edges of the drops run together, or by allowing a drop of the assay fluid to flow down over paper saturated with the indicating substance, etc.

c. In oxidizing or reducing the substance to be determined by means of standard solution without adding an indicator, the final reaction will be recognized by the appearance or disappearance of certain colors (chameleon

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1871. Rieth, Volumetrie, Bonn, 1871. Mohr, Titrirmethode, Braunschweig, 1874. Muspratt's Chemie, vii. 167.

assay), or by adding an indicator (starch in the assay of copper, assays of manganese, etc.).

The *operations* which may occur are as follows:—

a. Solution, that is to say, bringing the substance to be tested into a state of solution as in 1, *a* (p. 38).

b. Preparation of the standard solution, namely—

α. By dissolving a *weighed* quantity of a chemically pure solid substance, and diluting the solution to a definite volume, so that the chemical power of a unit of volume of the solution is known. These liquids are called *normal solutions* when as many grammes of the substance have been dissolved and diluted to 1 liter (1.76 pints) as are equal to the atomic weight of the substance, and *decinormal solutions* when a quantity of substance corresponding to $\frac{1}{10}$ of the atomic weight has been used for the solution.

β. By dissolving an *unweighed* quantity of the solid substance and making an *empirical solution* by diluting it in a corresponding manner, that is to 1 liter (1.76 pint). The titer of this is determined by allowing it to act upon a measured volume of a solution containing a known quantity of the body to be determined, until the reaction takes place. The titer is then found from the volume of the empirical solution consumed.

The standard (titer) of normal solutions subject to chemical alteration must be verified from time to time.

c. Measuring and titration of the assay liquid.—For this are required—

α. For measuring, *stoppered measuring flasks* (Fig. 18) divided up to a mark on the neck into 1, $\frac{1}{2}$, $\frac{1}{4}$ liter (1.76, 0.88, 0.44 pints) and into small divisions (200, 100 cubic centimeters, etc., 12.2, 6.1, etc., cubic inches); a *stoppered mixing cylinder* (commonly called a test-mixer) (Fig. 19), having a capacity of from one to two liters (1.76

to 3.52 pints), also divided into cubic centimeters. By means of this, fluids can be measured off, diluted, and mixed in definite proportions. *Pipettes* (*measuring-pipettes*) (Fig. 20), divided into whole and $\frac{1}{10}$ cubic centimeters; and *whole pipettes*, capable of holding a certain number of cubic centimeters up to a mark. The latter are used for transferring a certain quantity of assay fluid to a beaker glass, flask, etc. In doing this the lower end of the pipette is either held against the side of the vessel and the fluid allowed to run down on it, or it is held free. *Stohmann's siphon-pipette* is

Fig. 18.

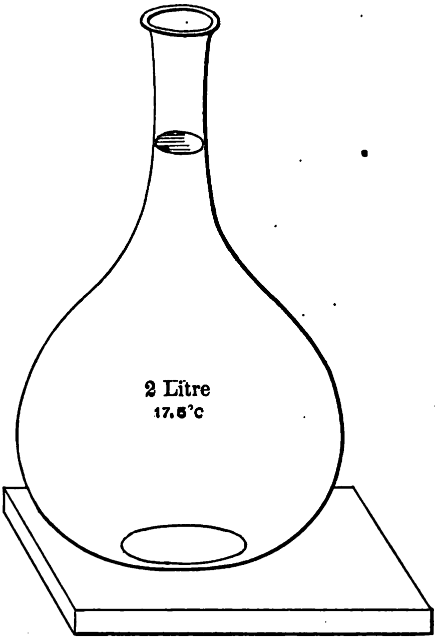


Fig. 19.

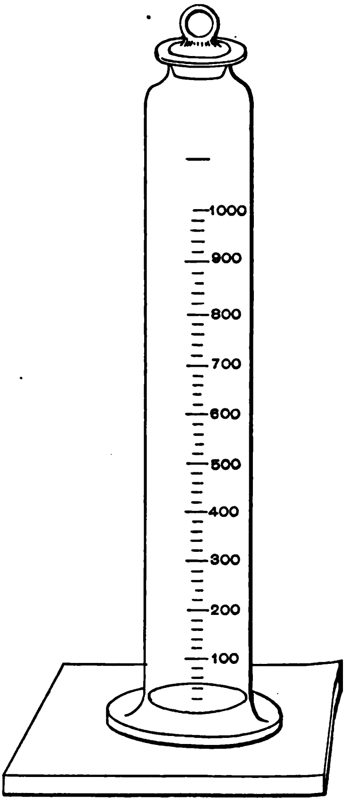


Fig. 20.

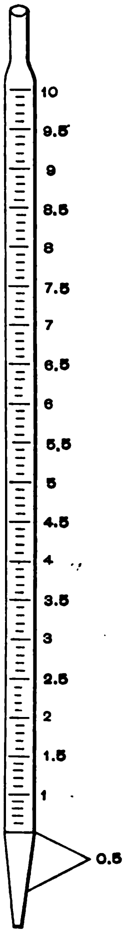


Fig. 21.

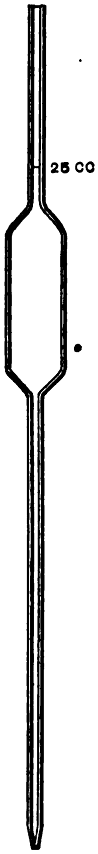
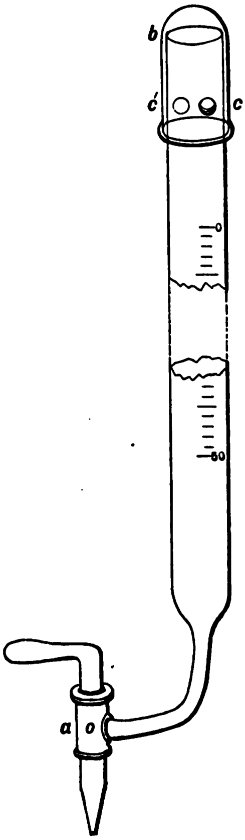


Fig. 22.



used for removing the clear supernatant liquid from precipitates, or poisonous, bad-smelling liquids, etc.

β. For titrating.—Burettes[1] for measuring the number

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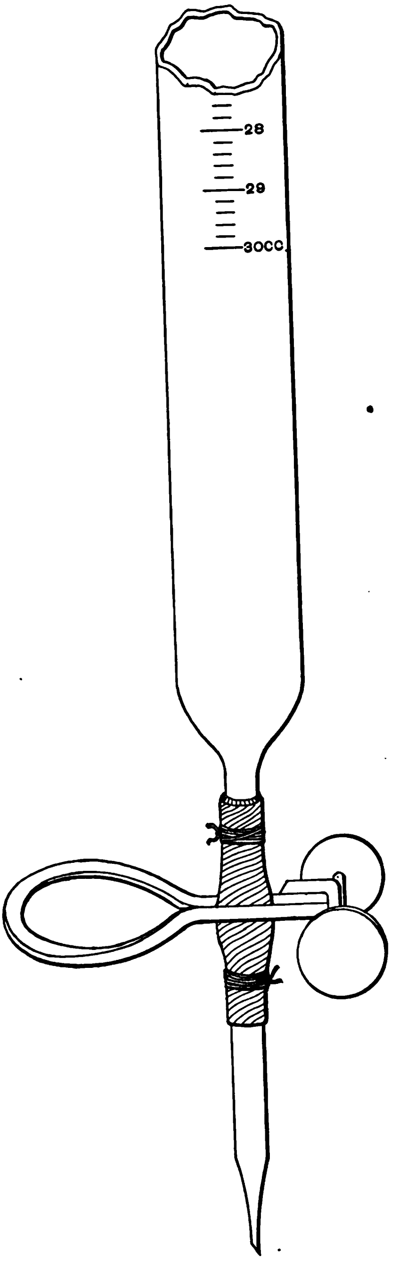
[1] Stender's glass manufactory in Lampspringe furnishes graduated glass vessels with graduation in red burned in with enamel. König's Ventilburette in Dingler, ccxvii. 134. Kleinert's Chameleon-burette in Fresenius' Ztschr. 1878, p. 183. Bürettenstative in Dingler, ccxxii. 465; ccxxix. 366. Fresenius' Ztschr. 1877, p. 82, 228.

Fig. 23.



of cubic centimeters of standard solution which have been allowed to run into the assay fluid until the final reaction is reached. For measuring assay and normal solutions, it is a very good plan to place two burettes in the same stand side by side. The burette represented by Fig. 22 (p. 47) is well adapted for all uses. It is provided with a glass cock *a*; *b* is a glass cap to protect the liquid from dust; *c c'* are openings in it for the admission of air. *Mohr's* burette is the simplest form of the apparatus, and has the preference over all others for general purposes. It is, however, not to be recommended in cases where the rubber of the pinch-cock will be liable to act chemically on the liquid employed. (Fig. 23.)

3. *Assays by colorimetric analysis.*—This method is based upon the principle that equal volumes of solutions of an equally intense color contain also equal quantities

of coloring matter. By comparing fluids of an equal intensity of color, and taking the volume into consideration, a conclusion is formed as to the percentage of the coloring body which is contained in the one to be determined. The same manipulations occur here as in assays by gravimetric analysis, namely, solution, precipitation, etc., and in addition comparison of the colored assay solution with standard colored solutions contained in tubes or tapering glasses of known cross-sections, measuring the solutions in calibrated cylinders, etc.

III. Assay Furnaces.

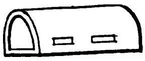
9. GENERAL REMARKS.

The choice of an assay furnace will depend chiefly on the degree of heat to be obtained, and whether the substances are to be oxidized or reduced, or only calcined, fused, sublimed, or distilled. Furnaces, accordingly, are divided into *muffle furnaces*, *draught* or *wind furnaces*, *blast furnaces*, *sublimation furnaces*, and *distillation furnaces*. In regard to their construction, they vary chiefly according to the fuel to be used (flaming or glowing fuel).

10. MUFFLE-FURNACES.[1]

The principal part of this is the muffle (Fig. 24). It is usually made of refractory clay, sometimes, though rarely, of iron. It is open in front, and closed at the rear; and the semi-cylindrical body is often provided along the sides with draft orifices, as shown. It is either connected

Fig. 24.



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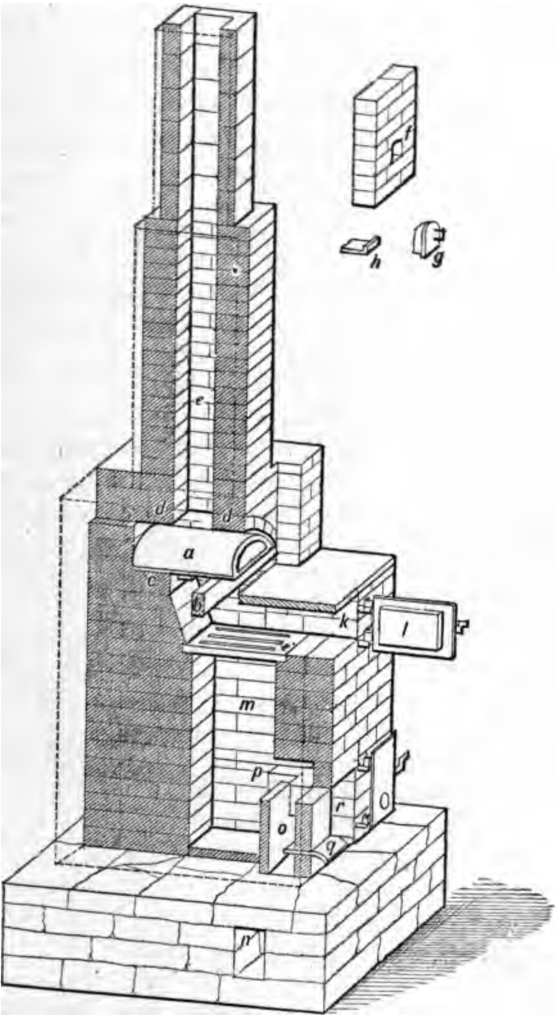
[1] Engin. and Min. Journ. 1878, No. 26, p. 443. Silliman, Double Muffle-Furnace, 1876, vol. xxii. No. 17.

with the bottom, or stands loose upon it. It serves for the reception of the assay charge, and is heated from the outside by a glowing or flaming fire. These furnaces are absolutely necessary for oxidizing processes (calcining, cupellation, refining), but they are also adapted for operations requiring only the production of a high temperature (glowing, reducing, and purifying fusion, etc.), that is to say, when only temperatures not exceeding the fusing point of gold and copper (about 1200° C., 2192° F.) are required (they are, therefore, not available for assays of cast iron). In the latter cases the fuel is not completely utilized, and besides, they are more difficult to attend than the wind and blast furnaces, where the crucibles, etc., are placed directly in the glowing fire, or come in direct contact with the flame.

The furnaces are either *bricked in* (for instance, large
muffle-furnaces for burning coal), or they are *portable*
In the latter case, the furnace for receiving the muffle
constructed of fire-clay which is sometimes surrounde
with a casing of sheet iron (mint furnaces). The wor
connected with the muffle-furnace consists chiefly in hea
ing it, regulating the temperature (by reducing or urgi
the fire, regulating the admission of air, opening or cl
ing the mouth of the muffle, by removing or piling
fuel, etc.), in stirring the fire regularly (in doing this
fuel must be piled chiefly upon the front part of the g
and only a thin layer upon the back part), in ventil
the grate frequently, in repairing (that is, lining def
places in the walls of the furnace, filling in of cra
the bottom of the muffle with fire-clay, or scrapi
bottom and lining it by strewing it with powder
clay, cupel ashes, chalk, pounded assay vessels, e
troducing and removing the assay vessels in the
cleansing the furnace after the work is finished

ing the glowing cinders from the grate and allowing the fire-door to remain open, etc.

Fig. 25.



According to the kind of fuel used, we may divide them into—

1. *Furnaces for solid, free-burning, flaming fuel.*—

These are generally used with large muffles, and with such fuel the heat can be better regulated than in furnaces heated by a glowing fire, but they require more care in attending them. Stoking is done from the front (*Plattner's* furnace[1]), or from the back (Schemnitz, Pribram[2]). With the latter arrangement the operator, working in front of the furnace, is not exposed to the direct heat, but it also prevents him from giving immediate attention to the firing should the assay require it.

Fig. 25 represents *Plattner's muffle-furnace for coal, with the stoke-hole in front.* *a*, muffle of fire-clay, 36.6 centimeters (14.4 inches) long, 17.6 centimeters (6.92 inches) high, and 34.2 centimeters (14.17 inches) wide, with an ascending slope of 2.4 centimeters (0.93 inch). It rests upon the support *b*, and three legs *c*; *d* is the vault. There is a space of 4.9 centimeters (1.92 inches) between it and the walls of the furnace. *e*, the chimney, 14.7 centimeters (5.73 inches) wide, and 3 to 4 meters (9.84 to 13.12 feet) high. *f*, mouth of the muffle, 12 centimeters (4.72 inches) wide, and 14.6 centimeters (5.74 inches) high, which can be closed by the fire-clay door *g*. Another door *h* is used for covering a slit sometimes provided over the muffle (for heating plates of metal, etc.), but it is usually omitted; *i* is the grate, 26.8 centimeters (10.55 inches) wide, and 51.4 centimeters (20.23 inches) long, 28.1 centimeters (11.06 inches) below the muffle; *k*, the stoke-hole, 22 centimeters (8.66 inches) high, and 26.8 centimeters (10.55 inches) wide; *l*, fire-door; *m*, ash-pit, 76.8 centimeters (30.25 inches) long, and 26.8 centimeters (10.55 inches) wide; *n*, a channel, 22 centimeters (8.66 inches) wide, communicating with the open air for conducting air under the grate through the flue *o*, *p*, 9.8 centimeters (3.85 inches) wide, which is provided with a damper *q*; *r*, ash-pit door, 26.8 centimeters (10.55 inches) wide, and 34.2 centimeters (13.46 inches) high.

Figs. 26 and 27 represent a *muffle-furnace with the stoke-hole at the back.* *a*, muffle, resting upon the supports *c* and *c'*; *b*, mouth of the muffle; *d*, front wall; *e*, grate; *f*, fire-door; *f'*, fire-box; *g*, refractory lining; *h*, *i*, channel for conducting the external air beneath

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[1] Freiberger, Jahrb. 1842, p. 1. Ztschr. des Ver. deutsch. Ingen. 1877, Plate 12, Figs. 3 to 5.

[2] Rittinger's Erfahr. 1857, p. 29. B. u. h. Ztg. 1876, p. 353; 1876, p. 61.

the grate; *k*, damper; *l*, ash-pit door; *l'*, ash-pit; *m*, fire-space surrounding the muffle; *m'*, chimney (it is better to place it nearer *d*), with damper *n*, *n'*, and lever *o*, for regulating the same; *p*, brickwork of the chimney, with flues *r*, for carrying off the fumes coming from the mouth of the muffle; *q*, hooping.

Fig. 26.

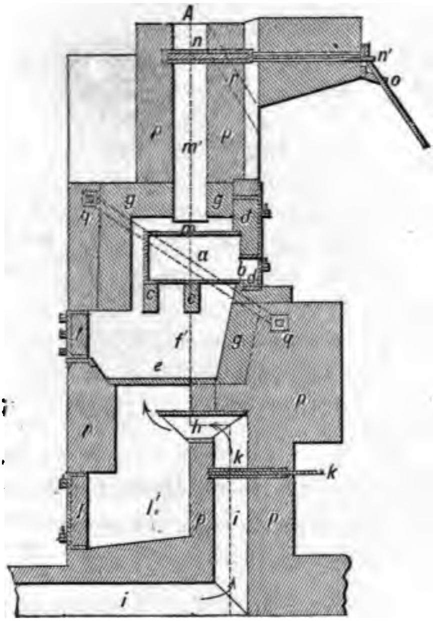
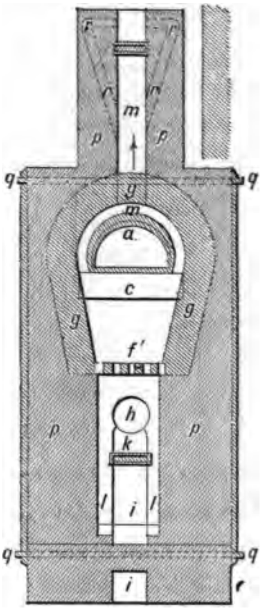


Fig. 27.

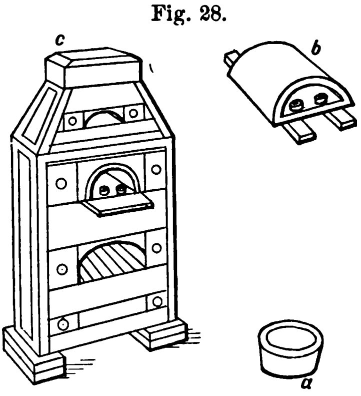


2. *Charcoal and coke furnaces.*—Coke as a general rule requires a grate under the muffle, and a strong draught. With charcoal this arrangement is not so essential, though in order to secure a more uniform supply of air a grate is usually provided. The ashes from coke are more difficult to remove and attack the walls of the furnace more than wood ashes. Smaller furnaces of this kind are much used for assaying gold and silver; and also larger ones, in which the heat can be better regulated (the Schemnitz charcoal furnaces are of this con-

struction), and where the stoke-hole is in the rear, or the firing is done through two channels on the sides.

Assay furnaces for charcoal. — Fig. 28 shows such a furnace. *b*, muffle of fire-clay, 14 centimeters (5.51 inches) long, 7.5 centimeters (2.95 inches) high, 9 centimeters (3.54 inches) wide, with walls 8 millimeters (0.31 inch) thick, and resting upon two rails passing through openings in the iron casing. The inside of the casing is lined with fire-clay from 15 to 20 millimeters (0.59 to 0.79 inch) thick. In front of the muffle is a shelf of sheet iron resting upon the rails supporting the muffle; *c* is the mouth of the furnace through which the charcoal is fed, and the products of combustion escape into a hood or through a sheet-iron smoke-stack. The mouth of the muffle and the flues above and below it can be closed by dampers; *a*, the cupel.

Fig. 28.

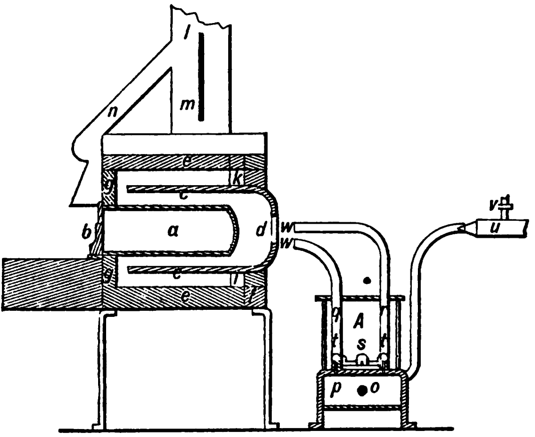


3. *Gas furnaces* (*coal-gas*).—By using these furnaces the work can be carried on in a very cleanly manner, and the temperature can be very perfectly regulated. The gas is introduced either by means of burners placed at the rear wall (*Perrot's* furnace, used in the Berlin School of Mines), or from below through four straight burners standing alongside each other beneath a slit in the bottom (furnaces of *Lenoir* and *Forster* of Vienna, used in the laboratory of the Schemnitz School of Mines, etc.), or through curved burners arranged in the form of a circle beneath the furnace (furnace of the Société genevoise pour la construction d'instruments de physique à Genève, used in the Berlin School of Mines). The oil furnaces of *Andouin-Deville* of Paris (using the vapors of crude petroleum) are said to be cheaper in operation than the

gas furnaces just described. The oil trickles from funnels upon the hot grate-bars set obliquely and channelled. There it is instantly vaporized and burns.[1]

Fig. 29 shows *Perrot's gas muffle-furnace*. *a*, muffle of fire-clay, with refractory coating and movable cover *b*; *e*, *f*, *g*, furnace walls of sheet iron with refractory lining; *A*, burner, with chamber *p*, into which coal gas enters at *o*, from the pipe *u*, provided with manometer *v*. From here it passes through narrow channels into the burner-tubes *q* and *r*, which are provided below with openings furnished with valves *t* for regulating the admission of air; *w*, *w*, the nozzles from which the flame passes through *d* into the space around the muffle, and escapes through the flue *k* into the chimney *l*, in which is a damper *m*. The chimney also receives, through the pipe *n*, the fumes which may escape from the mouth of the muffle.

Fig. 29.



11. DRAUGHT OR WIND FURNACES.

These consist—

1. In case *carbonized* fuel (coke, charcoal) is used, of a round, rectangular or oblong fire-place, separated from

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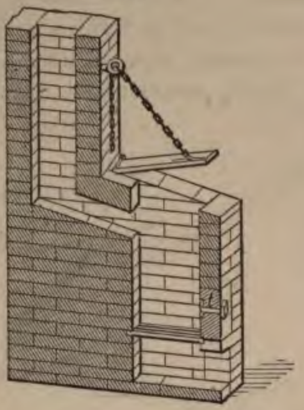
[1] Ztschr. des Ver. deutsch. Ingen. xxi. 225.

the ash-pit at the base by a grate, and provided with a fire-clay or cast-iron cover or top-plate. A lateral flue connects the fire-place with the chimney. The furnace is either bricked in (Fig. 30) or is portable. In the latter case, the body of the furnace is made of a sheet-iron cylinder lined with refractory material. It is also a very good plan to set a furnace of this kind into brick-work, leaving an intermediate space between the two, in which case the usual binding with strap-iron may be dispensed with. The cover or top-plate over the fire-place consists of two fire-tiles provided with some convenience for easily removing and replacing them. It is best to place a small carriage in the ash-pit for receiving and removing the ashes (Berlin School of Mines). The degree of temperature possible to attain, depends on the height of the shaft between the grate and the flue, the height of the chimney, and the quality of the fuel used (coke will give a higher temperature than charcoal). The temperature can be increased with the aid of a flue leading from the ash-pit into the open air, or by an under-grate blast, and is regulated by a damper fixed in the door of the ash-pit, or in the flue or chimney. The highest temperature is found at about 4 to 6 centimeters (1.57 to 2.36 inches) above the grate, which should be taken into consideration in placing the crucibles in the furnace.

Fig. 30.



The labor attending these furnaces consists of—

a. The placing of the assay vessels in the furnace by hand. If it is necessary to look into them during the operation (assay of lead in iron crucibles, Cornish roasting assay of copper), they are placed in a hollow made in the fuel, generally coke; or, if this is not required (assays for lead, copper, tin, iron, etc., in clay crucibles), the assay vessels are placed immediately upon the grate, leaving sufficient space between them for the necessary fuel, and in such a manner that the part of the vessel which is to be heated the strongest stands about 4 to 6 centimeters (1.57 to 2.36 inches) above the grate. If, therefore, vessels with feet are used, they must be placed directly upon the grate, while those without feet (crucibles) are supported on a block or stand of fire-clay.

b. Firing.—This, as a general rule, is done from *below* by putting glowing coals between the assaying vessels, filling up the shaft with fuel, and then gradually closing the top-plate of the furnace. But if the heating must take place very slowly, the firing is done from *above*, by placing the glowing coals on top of the fuel with which the shaft is filled. The fire, when the mouth of the furnace is closed, will then gradually work down. (In the Schemnitz laboratory, the lateral flue is placed below the grate and the air required for combustion is introduced from above.) The temperature is regulated in the manner indicated on p. 56, and, if necessary, fuel is added from time to time, but, before this is done, the glowing coal must be poked down to do away with empty spaces.

c. Taking the vessels from the furnace.—This is done by lifting the vessels out at the top of the furnace, by means of crucible tongs (Fig. 47), either out of the coke, or from the grate, after the fuel has burned down, or, in the latter case, it may be more convenient to remove them through an opening in the side (*t* in Fig. 30), but this must be closed up during the operation of the furnace.

Either the contents of the crucibles are poured out and the crucibles while still glowing placed back in the furnace and again charged from the mixing capsules (Fig. 6) (assay of lead in an iron crucible), or the clay crucibles are allowed to cool off and are then broken up.

A furnace for 10 *lead assays* is 35.4 centimeters (13.93 inches) high, 33.7 centimeters (13.26 inches) long, and 36.3 centimeters (14.29 inches) wide. It has seven bars. The door of the ash-pit is 15.3 centimeters (6.02 inches) wide, and 14.2 centimeters (5.58 inches) high, 14.2 centimeters (5.58 inches) below the grate. The chimney is from 1.75 to 2.34 meters (5.74 to 7.67 feet) high, with a diameter of 10 to 12 centimeters (3.93 to 4.72 inches). A furnace tapering towards the upper end and intended for 1 *lead assay* in an iron crucible has the following dimensions: 18 centimeters (7.08 inches) wide, 12 to 14 centimeters (4.72 to 5.51 inches) high, with walls 6 millimeters (0.23 inch) thick. The ash-pit is 12 centimeters (4.72 inches) high, and 14 centimeters (5.51 inches) wide. For *assays of copper*, the shaft of the furnace is a few centimeters higher and the chimney from 1 to 1.5 meter (3.28 to 4.92 feet) higher than that for lead. The Cornish furnace for assays of copper is 40 centimeters (15.74 inches) high, and 20 to 26 centimeters (7.87 to 10.23 inches) wide. For *iron assays*, the shaft is 55 centimeters (21.65 inches) high, and 33 centimeters (12.99 inches) wide. The ash-pit is from 29 to 30 centimeters (11.41 to 11.81 inches) high; the flue 33 centimeters (12.99 inches) long, and 11 centimeters (4.33 inches) high; the chimney 10 to 12 meters (32.8 to 39.37 feet) high, and 20 centimeters (7.87 inches) wide. The dimensions of the furnaces used in the Berlin School of Mines are: for assays of lead, 20 centimeters (7.87 inches) high, and 34 centimeters (13.38 inches) wide; for assays of copper, 26 centimeters (10.23 inches) high, and 34 centimeters (13.38 inches) wide; for assays of iron, 35.5 centimeters (13.97 inches) high, and 34 centimeters (13.38 inches) wide, with a chimney 10 meters (32.8 feet) high, provided with a damper for regulating the draught.[1]

2. *Wind furnaces for free-burning (flaming) coal.*—The assay vessels stand over the grate upon a tile of fire-clay in the same manner as in *Plattner's* furnace, except that there is no muffle. (Freiberg.)

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[1] B. u. h. Ztg. 1878, p. 83.

3. *Wind furnaces for illuminating gas.*[1]—These furnaces are easily attended, the work can be carried on in a ery cleanly manner, and at the same time with the reatest accuracy, as the assayer can conveniently look nto the crucible during the operation.

Fig. 31.

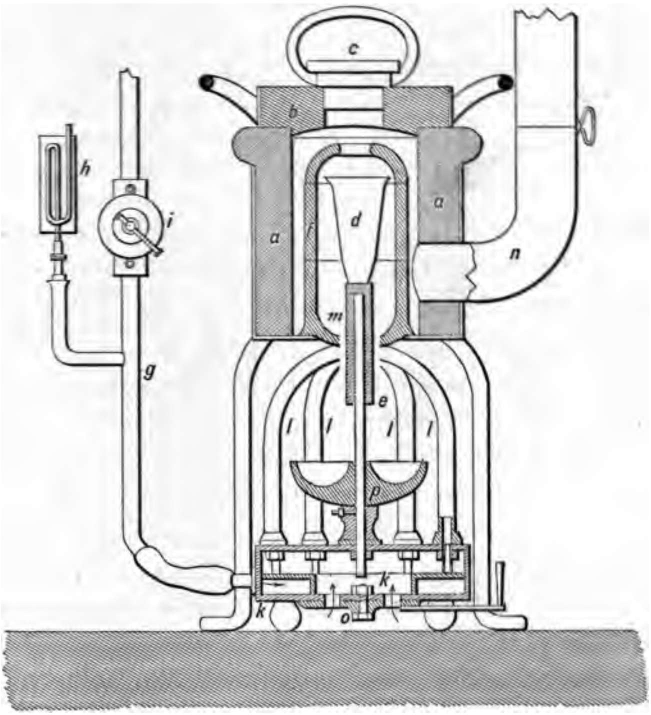

Fig. 31 represents *Perrot's furnace*. *a*, the outer shell, with cover , and sight-hole *c*; *d*, the crucible, upon a movable stand, *e*; *f*, inner hell; *g*, pipe, with manometer *h*, and cock *i*, for conveying gas into he annular chamber *k*, from which it passes through the pipes *l*, through the annular opening *m*, into the inner space of the furnace, where flame plays around the crucible *d*, and finally escapes through the upper opening of the inner chamber into the exterior annular space, and is carried off below through the pipe *n*, leading to the chimney; *o*, openings for admitting the air required for combustion, which is mixed in the pipes *l*, with the gas. The admission of air is regulated by a cut-off. *p* is a cup for the reception of any metal which may overflow and escape from the crucible.

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[1] B. u. h. Ztg. 1873, p. 284 (Perrot); Dingler, ccvi. 360 (Wiessnegg); ingler, clxxx. 220; clxxxix. 376; Oestr. Jahrb. v. Hauer, 1878, p. 123 Schlösing). Mitchell, Pract. Assaying, 1868, pp. 81 and 73. Hempel's asofen mit Oxydationsvorrichtung, z. B. zum Abtreiben, in Fresenius' Ztschr. xvi. 454; xviii. 404 (may be had of Desaga in Heidelberg).

Wiessnegg's gas furnaces are of simpler construction, and consume less gas. The flame plays around the crucible in the form of a spiral. By this means air and gas are more intimately mixed, and higher temperatures can be obtained. The same result is attained in Schlösing's furnace. The attainable heat of *Perrot's* furnace is about 1560° C. (2840° F.).

12. BLAST FURNACES.

These are low cylindrical shaft furnaces, constructed of fire-resisting material, or of a sheet-iron cylinder lined with refractory clay. At some distance above the hearth of the furnace, are one or several tuyeres symmetrically arranged. The mouth of the furnace is provided with a movable sheet-iron chimney. The furnace, in order to increase the temperature, is well supplied with air heated in the space between the two iron shells surrounding the shaft (*Sefström's* furnace) or in a reservior below the perforated hearth of the furnace (*Deville's* furnace).[1] The hearth in *Welch's* furnace may be easily separated from the furnace body.[2] The fuel used in these furnaces should be in lumps about the size of a walnut and uniform in size. A very high temperature can be produced in a shorter time, and with the consumption of less glowing fuel than in wind furnaces, but a certain amount of power is required for operating the blast (bellows, fan, Root's blower),[3] and the fire must be frequently stirred and fuel added. If only one crucible is used, it is placed in the centre of the furnace. But if more are placed in the furnace at one time, each is placed at the same distance from one of the tuyeres. *Raschette's* furnace furnishes very high temperatures; it has an oblong cross-section, and the tuyeres are arranged alternately in rows. *Munscheid's*[1] *gas blast furnace* gives also very high temperatures. Gas and air mixed, are drawn into it by means of an exhaust fan.

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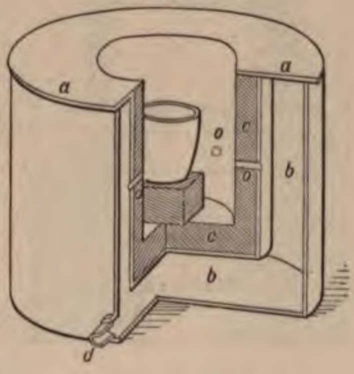
[1] Kerl, Thonwaarenindustrie, 1879, p. 65.

[2] Dingler, ccxxix. 159.

[3] Root's blowers are well adapted for this purpose.

Fig. 32 shows *Sefström's furnace.* *b* is the space between two sheet-iron cylinders closed on top by *a*. The inner cylinder is lined with a fire-resisting material, *c* (1 part clay and 3 to 4 parts quartz sand). The air enters at *d*, and, after having been heated in the intermediate space, is carried through the tuyeres *o*. The dimensions of a furnace for six small iron crucibles are as follows: 18 centimeters (7.07 inches) in diameter; total height 15 centimeters (5.9 inches); a collar 7 centimeters (2.75 inches) high, upon which sits the sheet-iron chimney; width and height in the clear, 10.5 centimeters (4.14 inches); thickness of the refractory lining 2.5 centimeters (0.98 inch); distance between the two cylinders, on the sides 1.2 centimeters (0.47 inch), and on the bottom 2.5 centimeters (0.98 inch). The manometer is placed on the exterior shell. *Lang's* blast-furnace[2] for larger masses has an annular air-conduit.

Fig. 32.



13. FURNACES FOR SUBLIMATION AND DISTILLATION.

These consist of a fire-space to be heated, for the reception of variously shaped vessels (tubes, retorts, boilers, etc.) of clay, porcelain, glass, or iron, in which the substances are heated without addition (as, arsenical pyrites, iron pyrites, amalgam), or with fluxes (preparation of realgar, separation of mercury from cinnabar, etc.). They are usually provided with a receiver, cooled off, for condensing the volatile products into solid bodies (sublimation), or to fluids (distillation).

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[1] B. u. h. Ztg. 1878, p. 361.

[2] Kärnthn. Ztschr. 1879, No. 8, p. 287.

Fig. 33 shows a *sublimation furnace*. *a* are clay tubes for the reception of the assay sample (as, for example, arsenical pyrites or iron and arsenical pyrites for the production of realgar); *b*, receiver for the sublimate (arsenic, realgar); *c*, the grate; *d*, flues.

Fig. 33.

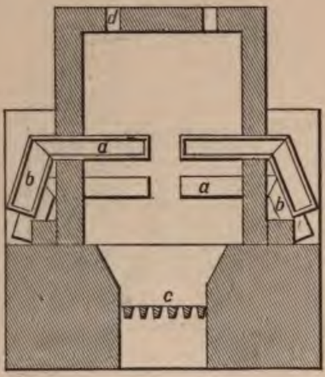


Fig. 34.

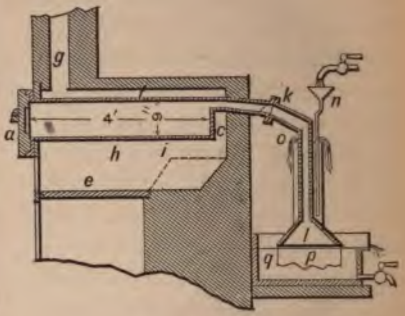


Fig. 34 represents a *distillation furnace*. *a*, tube for the reception of the assay sample (for instance, gold or silver amalgam); *e*, grate; *h*, combustion chamber; *g*, chimney; *c*, pipe for carrying off vapors (of mercury) into the condensing pipe *k*, provided with a funnel *l*, the edge of which is covered with a cloth *q*, upon which cold water flows from *n*, and overflows at *o*.—Or Fig. 35. *a*, a retort, with tubulure *b*; *c*, receiver, covered with paper or cloth kept cool by water which is allowed to trickle upon it.—Or Fig. 36, if a more thorough cooling off is required. *h*, a retort, from which the vapors pass through *i* into the cooling-pipe *a*. This rests upon a stand *g*, and is surrounded by a sheet-iron cylinder, into which cold water passes through *e*, and is discharged at *c f*, while the liquid formed from the condensed vapors is collected in *b*.

Fig. 35.

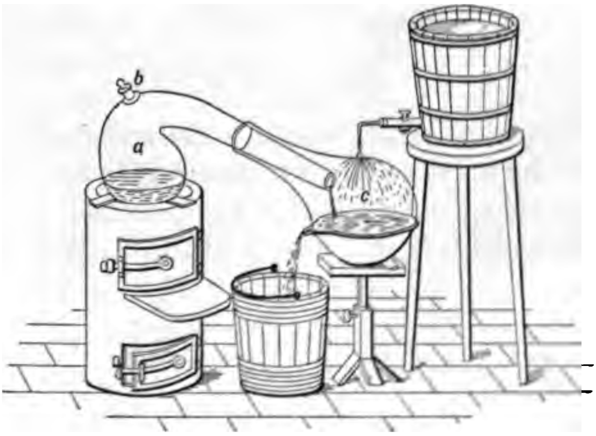
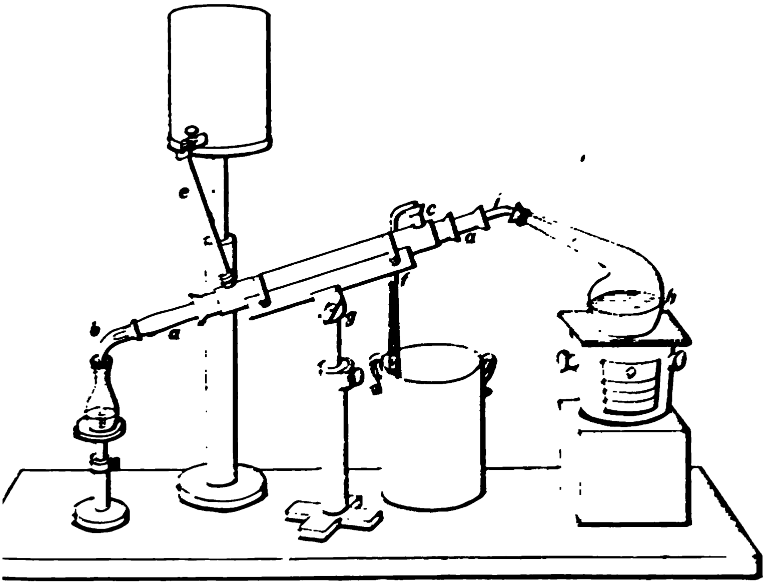


Fig. 36.



Organic-combustion furnaces (Fig. 38) may also be used for heating tubes.

IV. Assay Vessels.

14. GENERAL REMARKS.

The form of the assay vessels, as well as the materials from which they are made, varies according to the object for which they are to be used. The principal distinction is, whether they are to be employed in the *dry* or *wet* method.

15. ASSAY VESSELS FOR THE DRY METHOD.

A. Clay vessels.[1]—These are required to be more or less refractory according to the heat to which they are to be exposed (their refractory quality depends on the proportion between silicic acid and alumina and the quantity of fluxing agents—ferric oxide, lime, alkalies, magnesia—which may be present). They must allow of being suddenly heated and cooled without cracking (fat, contracting clay requires to be mixed with quartz, chamotte,[2] graphite). The vessels should be corroded as little as possible by the substances heated in them, but, as a general rule, this can never be entirely prevented. (It may be done to some extent by making the sides of the crucibles thicker, or by giving a finer grain to the stuff of which they are made. This should be made as compact as possible, by mixing the clay with chamotte instead of quartz. The interior of the crucible should be made very smooth, and it should be fired in the kiln as strongly as possible.) The vessels should further be very compact. This can be accomplished by giving a suitable grain to the mass, exercising great care in moulding and firing them strongly. The compactness of the vessels is tested by fusing metallic sulphides, such as galena, several times in them. They are made either by a *plug* and *mould* (roasting dishes and scorifiers, Upper Harz crucibles for lead smelting) or they are turned upon the potter's wheel (crucibles and larger melting pots).

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[1] Kerl, Thonwaarenindustrie, 1879, p. 491. Percy, Metallurgy, vol. I. 1875, p. 111.

[2] [Chamotte is a mixture of unburnt fire-clay and dust of fire-bricks, glass pots, or seggars.—TRANSLATOR.]

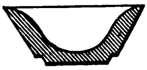
The principal vessels, etc., are—

1. *Vessels without feet.*

a. Roasting dishes (Fig. 7).—They are flat, smooth inside, not very refractory, 8 to 10 millimeters (0.31 to 0.39 inch) deep and 50 to 80 millimeters (1.96 to 3.14 inches) wide. They are used in the manner indicated on p. 34.

b. Scorification or calcining vessels (Fig. 37).—They have a thick bottom and sides, very smooth interior, and are very compact. To avoid being corroded by lead oxide, they should be made of clay mixed with chamotte. They are 40 to 50 millimeters (1.57 to 1.96 inches) wide in the clear, 15 to 20 millimeters (0.58 to 0.78 inch) deep, with a bottom 10 millimeters (0.39 inch) or more thick.

Fig. 37.



c. Refining dishes.—They have either the same form as the flat roasting dishes, but are fire resistant and one edge is somewhat ground down, or they are made from fragments (Fig. 38) of crucibles (Fig. 42), and are then 70 to 80 millimeters (2.75 to 3.14 inches) long; or they are shaped like a flat saucer with feet. These are 30 millimeters (1.18 inches) wide, with a total height of 25 millimeters (0.98 inch) (Hungary).

d. Crucibles.—These are of various forms and sizes, large and small (Figs. 39 to 41). They are respectively 32 and 45 millimeters (1.25 and 1.76 inches) high in the clear, and have a total height of 39 and 52 millimeters (1.53 and 2.04 inches), a clear width of 33 and 43 millimeters (1.29 and 1.68 inches), and are not very refractory. Fig. 40 shows a large and a small Cornish crucible for the assay of copper. They are very refractory. Their respective dimensions are: diameter on the top 80 and 68 millimeters (3.14 and 2.67 inches), total height 84 and 60 millimeters (3.3 and 2.36 inches). Fig. 41 represents a crucible for iron. This is lined by means of a wooden plug with charcoal powder *b* (this is first moistened with starch paste, molasses, or clay), or it is lined with a mixture of 90 to 95 per cent. retort graphite, 5 per cent. rosin, and some petroleum, and burned with exclusion of air. They are covered with the perforated lid *c*. They are 37 millimeters (1.45 inches) high and 25 millimeters (0.98 inch) wide, and, after they have been lined, respectively 22 millimeters (0.86 inch) and 10 millimeters (0.39 inch). They are very refractory (Hessian pots). The *French* pots are especially refractory and smooth inside.

Fig. 38.

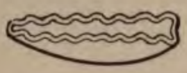


Fig. 39.

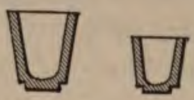


Fig. 40.

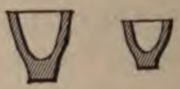
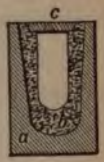


Fig. 41.



Graphite crucibles are made of graphite mixed with clay. They are very smooth inside, and very refractory. Those used in Cornwall for assays of tin are 80 millimeters (3.14 inches) wide on the top, and 50 millimeters (1.96 inches) on the bottom, have a clear height of 74 millimeters (2.91 inches), and a total height of 90 millimeters (3.54 inches).

Soapstone crucibles, if gradually heated, are adapted for all smelting purposes. They are infusible, not affected by alkalies, and become harder by burning.

2. *Vessels with feet. Crucibles for lead and copper smelting* (*a*, Fig. 42).—The latter are more refractory than the first. They are 25 to 32 millimeters (0.98 to 1.25 inches) wide on the top, 40 to 50 millimeters (1.57 to 1.96 inches) in the centre, 83 to 85 millimeters (3.26 to 3.34 inches) high in the clear, with a total height of 110 to 120 millimeters (4.32 to 4.71 inches). Sometimes there is a depression in the bottom for the reception of the regulus, and the foot, when broken off, may serve as a cover.

Fig. 42.

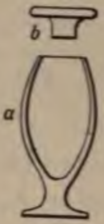
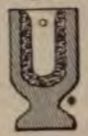


Fig. 43 shows a crucible for smelting iron, lined with powdered charcoal (see above). These crucibles are 45 millimeters (1.76 inches) wide, and 55 millimeters (2.16 inches) high in the clear, with a total height of 90 millimeters (3.54 inches).

Fig. 43.



3. *Other clay vessels.*—In this category belong *muffles* (p. 49), *retorts*, and *tubes*.

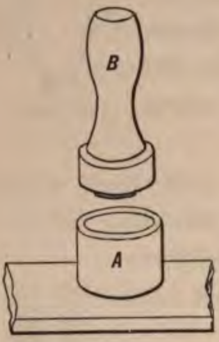
B. Wrought-iron vessels. Crucibles for assay of lead, with or without lip.—These are from 8 to 12 centimeters (3.14 to 4.72 inches) high, and 5 to 8 centimeters (1.96 to 3.14 inches) wide. The sides are from 10 to 12 millimeters (0.39 to 0.47 inch) thick, and the bottom from 2 to 3 centimeters (0.78 to 1.18 inches). Other iron vessels used are, *tubes* and *retorts*, and cast-iron *muffles*.

C. Vessels of bone-ash: Cupels (Fig. 44).—They are

Fig. 44.

made either of bone-ash alone, or with an addition of a little wood-ashes, or pearl-ash, to the water used for moistening the bone-ash, which addition decreases their power of conducting heat. The bones are burnt white throughout, are then powdered and washed. The dried powder, which should be about as fine as coarse wheat flour, is used for the principal mass, while a finer flour is reserved for a final coating. The cupels are formed by filling and driving the prepared bone-ash into a mould made for the purpose (Fig. 45), *B*, the pestle; *A*, the mould; or they are pressed.[1] Ordinary Freiberg cupels for ores consist of 3 volumes soap-boilers' ash, and 1 volume bone-ash. Their outer diameter is 35 millimeters (1.37 inches), diameter in the clear 24 to 25 millimeters (0.94 to 0.98 inch). They are 10 to 12 millimeters (0.39 to 0.47 inch) high in the clear, with a total height of 18 millimeters (0.7 inch). Fine or mint cupels consist of 2 volumes soap boilers' ash, and 3 volumes bone-ash. Their total diameter is 26 millimeters (1.02 inches), with a clear diameter of 18 millimeters (0.7 inch); their total height is 14 millimeters (0.55 inch). Cupels in order to be perfect should dry very slowly, and be thoroughly ignited before they are used. They should be white, and, besides a certain degree of solidity, should possess the requisite porosity to absorb litharge (when taken up with the tongs they must not crumble, but it should be possible to crush

Fig. 45.



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[1] B. u. h. Ztg. 1868, p. 154.

them with the fingers). They must neither undergo any perceptible change, nor crack, when exposed to a white heat, and should develop no gases and form no chemical combinations with the substances fused in them. When too solid they crack easily, absorb the litharge too slowly, cupellation being thereby prolonged, which causes a loss of silver. If, on the other hand, they are too porous, they absorb too much silver and gold with the lead oxides. (A loss of metal can never be entirely avoided in the assay.)

D. Vessels of other materials.—Cupels in the form of a prism about 2.5 centimeters (0.98 inch) high and 4 centimeters (1.57 inches) thick are chiselled out of charcoal, or turned from hard wood and then carbonized. *Coke cupels* are made of powdered and sifted coke, which is kneaded with liquid pitch. The stiff mixture formed after the mass has become cold, is pulverized, and some more powdered coke added to it (4 parts of coke to 1 part of pitch). The entire mass is then passed through a hair sieve, heated, and stamped in a cupel-mould about 2.5 centimeters (0.98 inch) high, with a diameter of 3.7 centimeters (1.45 inches) on the top and 3 centimeters (1.18 inches) on the bottom. The finished cupels are then ignited, the air being excluded during the operation.

16. ASSAY VESSELS FOR THE WET METHOD.

1. *For assays by gravimetric analysis.—Articles of glass:* digesting-flasks or matrasses, beaker-glasses, funnels, watch-glasses, wash-bottles, stirring-rods, retorts, tubes, apparatus for generating sulphuretted hydrogen, etc. *Of porcelain:* crucibles, evaporating dishes, tubes,

etc. *Of other materials:* forceps, crucible tongs, wire triangles, wire gauze, etc.[1]

2. *For assays by volumetric analysis,* see p. 43.

3. *For assays by colorimetric analysis.*—Tapering glasses or tubes of a uniform diameter for comparing colors; graduated measuring vessels of glass or porcelain, divided into centimeters, ounces, etc.; dissolving vessels, etc.

V. Balances and Weights.

17. BALANCES.

Of these will be required—

1. *An ore balance*, for weighing ores and the regulus of base metals. This should be capable of carrying from 30 to 50 grammes (1.05 to 1.76 ounces), and, with 5 grammes (77.19 grains) in each pan, must be distinctly sensitive to an addition of 1 milligramme (0.015 grain).

2. *Bullion or button balance*, inclosed in a case, for weighing gold and silver beads and alloys of precious metals. It should be capable of carrying 5 grammes (77.19 grains) at the utmost, and must distinctly turn with $\frac{1}{10}$ to $\frac{1}{20}$ milligramme when both pans are loaded with 1 gramme (15.43 grains).

3. *An apothecary balance*, for weighing larger quantities. It should be sensitive to 5 milligrammes (0.077 grain).

4. *A rough scale*, for weighing approximately larger quantities (fluxes, etc.). A grocer's scale will answer the purpose.

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[1] Muencke's Klemmvorrichtung in Dingler, ccxxv. 387. Dreiecke und Tiegelzangen mit Porzellanarmirung in Fresenius' Ztschr. 1879, p. 259. Doppelaspirator, Dingler, ccxxv. 619.

18. WEIGHTS.

The following are used:—

1. *The gramme weight*, from 50 to 0.001 gramme (771.61 to 0.015 grains); for silver coins from 1 gramme (15.43 grains)=1000 parts to $\frac{1}{10000}$ part; for assays of gold from $\frac{1}{2}$ gramme (7.71 grains) as the unit = 1000 parts to $\frac{1}{10000}$ part.

2. *Centner.*—1 assay centner = 5 grammes (77.19 grains) (Upper Harz) or = 3.75 grammes (57.89 grains) (Freiberg) = 100 pounds, which is divided into 100 parts of pounds, or the *quint*, the smallest weight being $\frac{1}{2}$ of the quint.

In *Austrian* smelting works, etc., 1 assay centner = 10 grammes (154.38 grains), which is divided into 100 parts, called pounds; the pound is divided into 32 loth, the loth into 4 quentchen, and this into 4 denär, the smallest weight being 1 denär — 0.195 milligramme (0.003 grain).—*English grain weight.* The unit is usually 1000 grains (64.8 grammes). The smallest weight for gold and silver buttons is 0.001 grain. For an assay of ore, generally a sample is taken weighing 400 grains. The divisions of this system are as follows: 1 ounce = 480 grains = 20 pennyweights (24 grains to the pennyweight).—*American assay weight.* 1 assay ton = 29.166 grammes (450.26 grains); 1 pound avoirdupois (commercial weight) = 7000 troy grains (apothecaries' weight); 1 ton = 2000 pounds avoirdupois; 2000 × 7000 = 14,000,000 grains troy in 1 ton avoirdupois; 480 grains troy = 1 ounce troy; 14,000,000 ÷ 480 = 29,166 troy ounces in 2000 pounds avoirdupois; one assay ton contains 29,166 milligrammes, therefore, 2000 pounds are to 1 assay ton as 1 ounce troy weight to 1 milligramme (0.015 grain). If, for instance, an assay ton yields 1 milligramme (0.015 grain) of gold or silver, the result will be 1 ounce troy in 2000 pounds avoirdupois without further calculation.

[For general practice, it is far preferable to use the French metric system of weights, instead of the arbitrary and varying German systems. The simplicity and convenience of the American assay ton leaves nothing to be desired.—TRANSLATOR.]

VI. Tools and Implements.

19. GENERAL REMARKS.

We will only consider the tools and implements required for the *dry method*, as those for the *wet method*[1] do not differ from those used in analytical chemistry (stands, forceps, crucible tongs, cork drill, etc.).

20. FURNACE TOOLS.

The following tools are used in attending the furnaces. *Shovels* with perforated blades for handling the fuel; large and small *iron pokers* and *scrapers* for cleansing the grate and muffle, poking the coal, etc.; *coal* and *ash sieves* with meshes respectively 1 centimeter (0.39 inch) and 3 millimeters (0.11 inch) wide; *iron boxes* filled with water for cooling the tools, etc.

21. IMPLEMENTS.

The following are required:—

A. For preparing the assay sample.

1. *Sampling.—Iron spoons* having a diameter of 4 centimeters (1.57 inches); *shovels; troughs, wooden boxes, etc.*, for the reception of the assay samples; *files* and *cold chisels; hollow chisels; drills; hollow cylinders of sheet iron* for small ore; *magnifying glass*, etc.

2. *For drying the samples* (p. 26).—*Drying pans* of sheet iron or copper; *drying frames; iron spatulas; dry-*

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[1] Neuere Geräthschaften in Fresenius' Ztschr. f. analyt. Chemie.

ing disk (Fig. 2, p. 26); *water-baths* (Fig. [illegible], p. [illegible]); [illegible] *baths* ; *desiccators* (Fig. [illegible], p. 43), etc.

3. *For comminuting the samples* (p. 21).—*Crushing plate* and *rubber* ; *mortars* ; *hammers* ; [illegible] ; [illegible] ; *common scissors* and *plate shears* ; *files* ; *rasps* ; *pliers* ; *vise*, etc.

4. *For sifting.*—A series of sieves of from 20 to 100 meshes to the inch, for sifting ores, fluxes, etc. A box sieve, consisting of a round tin box, into which a sieve can be snugly fitted, is very useful, as in sieving the pulverized ore there is no dust. If desired, a tin cover can be made to inclose the whole.

5. *For washing* (p. 28).—*Beaker glasses* ; *glass cylinders* ; *wooden vanning troughs* (Fig. 4, p. [illegible]), etc.

6. *For weighing.*—*Brass pincettes* with fine ivory points for taking up small weights, metal buttons, etc., and others with blunt or broad points for lifting larger weights and heavier buttons of precious and base metals; *brass mixing spoons*, 18 centimeters (7.08 inches) long and 2 centimeters (0.78 inch) wide, having on one end a *spatula* [illegible] centimeters (0.[illegible] inch) wide; *camel's-hair* and [illegible] *brushes* ; *watch-glasses* ; *small glass or porcelain* [illegible] ; *glass tubes*, one end closed and the other closed with a cork or glass stopper; *glazed paper* [illegible] ; *cornets* of fine letter-paper of different colors [illegible] for the reception of charges [illegible]

7. *For charging.*—[illegible] mixing *spatula* of [illegible] *ing spoon* for granulated [illegible] *dles*, etc.

8. *Implements* [illegible] *for manipulating* [illegible] (Fig. 46) for storing [illegible] muffle-furnaces [illegible]

39.37 inches) long, and, for smaller furnaces, 50 to 60 centimeters (19.68 to 23.62 inches). Scorification tongs with one arm forked, as shown in Fig. 46*a*, the horseshoe part just large enough to fit the scorifier, 60 millimeters (2.36 inches) long and 45 millimeters (1.76 inches) wide; *crucible tongs* (Fig. 47) for wind and blast furnaces. Small *assay plates* of sheet iron, with handles. They are about 14 centimeters (5.5 inches) square, and are provided with 9 depressions each 28 millimeters (1.1 inches) wide, in which cornets, simple weights of lead (Bleischweren), etc., are kept. The following implements are required for manipulations in the furnace during roasting, fusing, etc.: *curved stirring rods* and *spatulas* of iron; *iron ladles*; *tongs* with curved tips (Fig. 46*b*) for taking hold of cornets, buttons, etc.; *cooling iron* (Fig. 48). The blade of this for large muffle-furnaces is 9 centimeters (3.54 inches) long, 7 centimeters (2.75 inches)

Fig. 46.

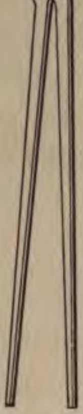


Fig. 46*a*.

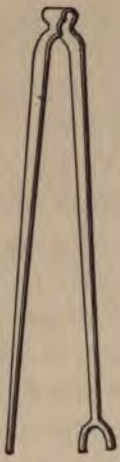


Fig. 46*b*.

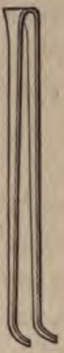


Fig. 47.

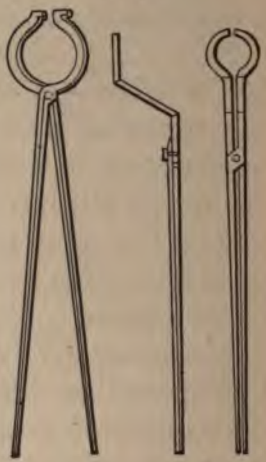
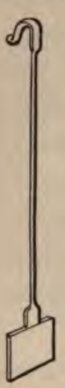


Fig. 48.



[illegible] 1 centimeter ([illegible] inch) thick. It is provided [illegible] centimeters (33.4 inches) long. [illegible] the respective dimensions are [illegible] centimeters ([illegible] inches), [illegible] and 70 centimeters ([illegible] inches). *[illegible] required for the reception and further [illegible] samples after they have been taken [illegible]*

[illegible] *the assay samples are required* [illegible] with handle. They are divided into [illegible] of sheet iron crossing each other, [illegible] compartments about 4 centimeters ([illegible] inches) [illegible] the assay vessels are placed. [illegible] for casting lead and silver bars [illegible] or *leaden plates* (Kornbleche) [illegible] centimeters (3.93 inches) long and 60 millimeters [illegible] wide, with depressions 1 centimeter [illegible] for the reception of gold and silver [illegible] the cupels; and *boards of wood* with [illegible] the reception of buttons of base metals.

[illegible] of the samples [illegible] —*Hammers* for breaking the clay crucibles and removing the slag from the button. The [illegible] is about 9 centimeters ([illegible] inches) long, [illegible] the other end running into a point [illegible] hammers; an *anvil* with a plate [illegible] centimeters square (2.36 inches) [illegible] centimeters ([illegible] inches) long, for [illegible] buttons of silver and gold from the cupels; [illegible] consisting of a brass holder with bristles [illegible] *magnet* for extracting particles of [illegible] g, etc.

VII. Assay Reagents.

22. REAGENTS[1] FOR DRY ASSAYS.

According to their action they may be divided into—

1. *Reducing agents.*—*Charcoal* in the form of powder, or of small pieces placed on top of the charge (assays of lead, copper, etc.), or of crucible lining (assays of iron); when it is generally mixed with other reducing agents (potassium carbonate, sodium carbonate, etc.), because the presence of a large percentage of charcoal without additions in smelting processes renders the charge more difficultly fusible.

Powdered coke, anthracite, and graphite[2] may also be used instead of powdered charcoal, but they are less combustible. Rosin, fat oils, tallow, sugar, etc., were formerly also employed. Bitartrate[3] of potassium (argol) ($KC_4H_5O_6$), either crude or refined, yields considerable carbon in becoming carbonized, and in consequence exerts a vigorous reducing effect, but causes refractoriness. For this reason its percentage of carbon is reduced, if necessary, by mixing it in different proportions with saltpetre. The mixture is poured into a red-hot crucible, placed under a well-drawing chimney. The mixture deflagrates and emits empyreumatic vapors, when, by reason of a partial oxidation of the carbon, a mixture of potassium carbonate and carbon is formed. This is known as *black flux*. For vigorous reduction it is made from 1 part of saltpetre and 3 parts of argol; for less vigorous, either of 1 and 2½, or 1 and 2 parts respectively. Another flux containing potassium carbonate (without carbon), mostly with undecomposed saltpetre, and known as *white flux*, consists of 1 to 2 parts of saltpetre, and 1 part of argol; *gray flux* has 3 of argol to 2 of saltpetre. A mixture of argol and saltpetre, before it is deflagrated, is called *raw flux*. As black flux, on account of its hygroscopic properties, must be frequently prepared fresh, and this work is unpleasant by reason of the evolution of bad odors, a mixture of potassium carbonate (or soda) and flour (starch $= C_6H_{10}O_5$), which is also cheaper, is used in preference. Usually 20 to 25 per cent. of wheat flour is taken, but for more vigorous reductions 30 to 35 per cent. (for instance in assays of copper), and even as much as 50 per cent. (assay of tin). When this mixture is used, a separation of carbon, in a fine state of division, takes place, with the exhibition of a yellow flame of carburetted hydrogen, caused by the carbonization of the flour during the fusing of the assay sample. The flame of the carburetted hydrogen must not be confounded with the *blue flame* of carbonic oxide. Mixtures of potassium carbonate (or of sodium carbonate) and coal-dust are less intimate, and their action is consequently less energetic than that of mixtures in which the carbon has been separated from organic substances in a very finely divided condition (tartaric acid, flour). *Potassium cyanide*, with 64.1 K and 35.9 Cy, is an energetic reducing (also desulphurizing) agent, even at a low temperature (assays of tin). *Potassium ferrocyanide*, $K_4Fe(CN)_6$, yields, on heating, a mixture of iron carbide, ferrous and ferric oxides, free carbon, and a small quantity of potassium cyanide. It has also a vigorous desulphurizing action.

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[1] Muspratt's techn. Chemie, 3d Aufl. Bolley, Handb. der techn. chem. Untersuchungen, 1879.

[2] Werthbestimmung in Fresenius' Ztschr. 1875, p. 394.

[3] Werthbestimmung in Fresenius' Ztschr. vii. 149.

The reducing power is estimated from the quantity of lead which is yielded by fusing 1 to 2 grammes (15.43 to

30.87 grains) of the reagent with 60 grammes (926.30 grains) of litharge and 15 grammes (231.48 grains) of sodium carbonate or potassium carbonate.

According to *Berthier* the reducing power of the various agents is as follows: 1 part hydrogen, 104; pure carbon, 34.31; well-glowed wood charcoal, 31.81; ordinary wood charcoal, 28.00; tallow, 15; sugar, 14.5; kiln-dried starch, 13; ordinary starch, 11; tartaric acid, 6; oxalic acid, 0.90; black flux with 2 parts of argol, 1.40; black flux with 2½ parts of argol, 1.90; black flux with 3 parts of argol, 3.80; 94 parts soda and 6 wood charcoal, 1.80; 88 parts soda with 12 charcoal, 3.60; 90 parts of soda with 10 of sugar, 1.40; 90 parts of soda with 10 of starch, 1.15; 80 parts of soda with 20 parts of starch, 2.30; crude argol, 5.60; purified argol, 4.50; pure argol (carbonized), 3.10; potassium binoxalate (salt of sorrel), 0.90; white soda-soap, 16 parts.

2. *Oxidizing agents.*—*Saltpetre*, KNO_3, with 46.56 K_2O, and 53.44 N_2O_5. It should be as free from sulphates as possible.—*Litharge*, PbO, with 92.83 Pb, and 7.17 O, exerts an oxidizing effect upon metals and metallic sulphides (scorification), as well as upon organic substances (assay of fuel). As generally used it is in the form of red litharge free from particles of metallic lead.[1] It should completely dissolve in acetic acid, and be as free from gold and silver as possible. When it contains silver, *white lead* not adulterated with heavy spar, $2(PbCO_3)+Pb(HO)_2$, with 86.27 PbO, may be substituted for it. It is best to prepare this by the wet method (for instance, by that of *Dietel*, of Eisenach, which yields a product free from gold, silver, antimony, and copper).

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[1] Dingler, cxciv. 84.

According to *Berthier*, 1 part of the various metallic sulphides requires the following quantities of litharge for its decomposition :—

	Parts.
PbS	1.87
HgS	10 to 12
BiS	20
Sb_2S_3	25
ZnS	25
FeS	30
SnS_2	25 to 30
Copper pyrites	30 to 35
FeS_2	50
As_2S_3	50 to 60

Litharge entirely free from silver can be prepared by oxidizing the purest *Pattison* or *Villach* lead by cupellation, or bringing such lead, after it has been granulated, into fused saltpetre; or by gradually strewing charcoal powder upon litharge fused in a refractory crucible, whereby some lead will be reduced which, in sinking down, withdraws the silver from the litharge.

3. *Solvent agents.*

a. Acid; such as powdered quartz; powdered glass[1] free from arsenic and lead. It should contain 60 to 70 per cent. or more of SiO_2, 5 to 22 per cent. of alkalies, 6 to 25 per cent. of lime, 0.5 to 5 per cent. alumina, and its fusing point should be between that of borax and fluorspar, or about 1200° C. (2192° F.). *Borax*, $Na_2B_4O_7+10H_2O$, with 16.37 Na_2O, 36.53 BO_3, and 47.10 H_2O. It should be completely dehydrated, or in the condition known as *borax-glass.* This is produced by fusing borax in a clay crucible, and then pouring it upon a bright metallic surface. It is more fusible than glass, and the boracic acid forms combinations with nearly all the bases as well as with silicic acid. *Salt of phosphorus* (*sodium-ammonium-hydrogen phosphate*), or *microcosmic salt*,

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[1] Analyses of Glass, in Poggendorf's Ann. 1879, vol. 6, p. 431. Dingler, ccxxxii. 348 (Weber).

$NaH(NH_4)P + 4H_2O$, with 14.90 Na_2O, 12.46 NH_4O, 4.29 basic water, and 34.32 water of crystallization, and 34.03 P_2O_5. In the anhydrous condition it is a more energetic solvent agent than borax (assays of cupreous nickel). *Clay*, such as kaolin, $Al_2Si_2O_7$, with 46.40 SiO_2, 39.68 Al_2O_3, 6.96 H_2O, and 6.96 *aq.*; burned China clay contains 53 Si_2O_2 and 47 Al_2O_3. Most varieties of clay contain over 50 per cent. of silicic acid.

b. Basic; such as *potassium carbonate*, K_2CO_3, with 68.09 K_2O and 31.91 CO_2. It should be as free as possible from sulphates, and, when mixed with carbon as *black flux* (p. 76), and with flour (p. 77), is a vigorous reducing, fluxing, and desulphurizing agent. *Sodium carbonate*, Na_2CO_3, with 58.58 Na_2O and 41.42 CO_2, acts somewhat less energetically than potassium carbonate, and consequently a larger quantity of it must be used. It is less deliquescent, more fusible, and cheaper. A mixture of 13 parts of dry potassium carbonate and 10 parts of calcined sodium carbonate, furnishes a flux very easily fusible.—*Caustic alkalies* act more energetically than carbonates, but exert a very injurious effect upon the crucibles.—*Calcium carbonate*, $CaCO_3$, with 56.29 CaO, in the form of chalk (or calcite), may be used for smelting operations at higher temperatures (for instance, in assays of iron, Cornish assays of copper).—Fluor-spar (*calcium fluoride*), $CaFl_2$, with 51.54 Ca, is more easily fusible than calcium carbonate, and is especially effective for removing silicic acid. It readily fuses down with calcium phosphate, heavy spar, and gypsum.—*Lead oxide* (litharge, minium, white lead) readily fuses with silicic acid, the alkalies, and with most of the heavy metallic oxides, but less so with the earths and alkaline earths.—*Ferric oxide*, F_2O_3, with 69.3 Fe (in assays of copper).

4. *Precipitating or desulphurizing agents.*—*Iron* in the form of iron filings (assays of zinc blende, antimony, and murcury), and as pieces of wire 4 to 5 millimeters (0.15 to 0.19 inch) thick, 6 to 9 millimeters (0.23 to 0.35 inch) long, and weighing from 0.5 to 2 grammes (7.71 to 30.87 grains) (assays of lead and bismuth).—*Potassium cyanide* (p. 77) and *potassium ferrocyanide* (p. 77). The *caustic alkalies* and *carbonates* (p. 80) decompose metallic sulphides. The metal is separated, and sulphites, hyposulphites, and sulphates of the alkalies together with alkaline sulphide are formed. The latter forms a sulpho-salt (for instance, with FeS, PbS, and Cu_2S) with one part of the metallic sulphide, which, as a general rule, can be decomposed with iron. Carbon promotes desulphuration (*black flux*, *potassium carbonate*, and *flour*, p. 76).—*Lead oxide* (p. 78).—*Saltpetre* oxidizes metallic sulphides, while the metals (silver, copper, lead) are separated.

5. *Sulphurizing agents.*—*Sulphur* in the form of flowers of sulphur; or of *iron pyrites* (Cornish assay of copper).

6. *Concentrating fluxes.*—*Lead* in a granulated condition (assay lead). It is prepared by rocking lead in the form of thick liquid paste in a trough well covered with chalk and then sifting the mass. It is also used in the form of sticks of the purest *Pattison* lead for alloying with gold and silver. (Where the assayer is obliged to make his own granulated lead, as in sections where pure lead free from silver cannot be obtained, it will be necessary for him, after granulation in the manner above described, to sample well, and test about 30 to 50 grammes for silver by the scorification assay. In using this lead, the amount of silver contained in it must, in all cases, be deducted from the results obtained in making an assay.)—

Silver[1] for alloying with gold (quartation).—*Gold* for collecting copper (assay of nickel and cobalt).—*Antimony* (*antimony oxide*) and *arsenic* for copper (refining).—*Copper oxide* for tin.—*Iron pyrites* as a collecting agent for copper (assay of matt).

7. *Decomposing and volatilizing fluxes.*—*Charcoal* and *graphite* for decomposing sulphates, arseniates, and antimoniates by roasting.—*Ammonium carbonate* $(NH_4)_2CO_3$ for decomposing sulphates, especially copper sulphate, at red heat (p. 35), but less completely lead and bismuth sulphates.—*Common salt* (*sodium chloride*) $NaCl$, with 39.66 Na and 60.34 Cl, for the volatilization of antimony and arsenic in refining black copper according to the Cornish method.

8. *Air-excluding fluxes* (covering agents).—*Decrepitated common salt*, as free from sulphates as possible, fuses easily, and, becoming very thin fluid, washes down particles of metal adhering to the sides of the assay vessels. It volatilizes at a red heat.—*Glass* (p. 79) in *Berthier's* assay of fuel and assay of matt.—*Refined slag* from charcoal iron blast-furnaces (in assays of zinc).

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[1] *Preparation of pure silver:* Cupreous silver or fine silver is dissolved in pure nitric acid. This is diluted with distilled water, allowed to stand for some time, and then filtered. The filtrate is strongly diluted, and chloride of silver is precipitated by the addition of pure hydrochloric acid. This is washed by decantation and then boiled several times with diluted hydrochloric acid, but after each boiling it should be washed with distilled water. The moist chloride of silver (3 parts) is mixed with dry sodium carbonate (1½ parts) and with pure saltpetre (¼ part of the whole) The mixture is then dried in a porcelain dish and fused in a porcelain crucible; or 100 parts of chloride of silver are fused with 70 parts of chalk, and 4 parts of wood charcoal. (Mohr, Titrirmethode, 1874, p. 425. Fresenius' Ztschr. xiii. 179.)

23. REAGENTS FOR WET ASSAYS.

The following are principally used.

1. *For assays by gravimetric and colorimetric analysis.*—*Acids:* hydrochloric, sulphuric, nitric, and acetic acid, aqua regia (nitro-muriatic acid). *Bases and salts:* caustic alkalies, alkaline carbonates, potassium chlorate, ferrous sulphate, sodium sulphide, etc.—*Metals* for precipitation: *iron* in the form of wire-pins 30 to 35 millimeters (1.18 to 1.37 inches) long and 2 to 3 millimeters (0.079 to 0.12 inch) thick, or in a pulverulent condition, for copper; *zinc* in the form of such pins or of granules or in a pulverulent state,[1] as a reducing agent for iron solutions, etc.; *copper* (electrolytic copper is the purest); *bromine*[2] for decomposing sulphurets, compounds of gold, etc.

2. For volumetric assays: *Potassium permanganate* (chameleon), $KMnO_4$, with $29.8\,K_2O$ and $70.2\,Mn_2O_7$; *sodium sulphide; potassium cyanide; barium chloride; potassium iodide*, free and with dissolved iodine; *sodium hyposulphite; ferric chloride; sodium chloride; potassium sulphocyanide*, etc. As indicators: *litmus tincture, tincture of Brazil wood*,[3] etc., for acids and alkalies; for sulphur: *the salts of iron, nickel, and lead*, and *sodium nitroprusside;* for iodine: *starch paste;* for iron oxide: *potassium sulphocyanide*, etc.

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[1] Dingler, ccxxviii. 378.

[2] Dingler, ccxix. 544.

[3] Fresenius' Ztschr. 1875, p. 324 (Rothholz). Bericht der deutsch. chem. Ges. 1876, p. 1572 (Fluorescein).

SPECIAL DIVISION.

I. LEAD.

24. LEAD ORES.

Galena (*lead monosulphide*) PbS, with 86.6 Pb; *cerusite* (*lead carbonate*) $PbCO_3$, with 76.6 Pb; *anglesite* (*lead sulphate*) $PbSO_4$, with 68.3 Pb; *pyromorphite* $3Pb_3P_2O_8+PbCl$, with 76.3 Pb; *crocoisite* (*lead chromate*) $PbCrO_4$, with 63.2 Pb; *wulfenite* (*molybdate of lead*) $PbMoO_4$, with 57 Pb.

25. ASSAYS OF LEAD IN THE DRY WAY.

The results of these assays are inaccurate, as the lead is liable to slag off and to volatilize, which is promoted by the presence of other volatile substances (arsenic, zinc, antimony), and also by reason of a possible contamination of the lead by other metals (copper, arsenic, antimony, bismuth). The highest yield which can be obtained from pure galena is 85.25 per cent., but in poorer ores the loss of lead may be 5 per cent. greater. The results are sometimes calculated to whole per cents., but more frequently from 5 to 5 per cent.

The condition of the ore, whether the lead is sulphurized or oxidized, and whether the substance is pure or contains more or less of earths and foreign metallic sulphides, will decide the choice of the assay method.

I. *Sulphurized Substances.*

A. Gelena, etc., without foreign metallic sulphides (ZnS, FeS, Cu_2S, Sb_2S_3, As_2S_3).—*Precipitation assay:* the assay sample is either decomposed by alkalies alone (Upper Harz assay with potassium carbonate, assay with potassium cyanide), or together with metallic iron (in an iron pot or clay crucible), with the following *reactions:*—

The lead sulphide is decomposed by the alkalies at a comparatively low temperature ($7PbS + 4K_2CO_3 = 4Pb + 3(K_2PbS_2) + K_2SO_4 + 4CO_2$). The sulpho-salt ($K_2PbS_2$), which otherwise would pass into the slag, is either decomposed by iron at a high temperature, $3(K_2PbS_2) + 3Fe = 3Pb + 3(K_2FeS_2)$, or, as is the case in the Upper Harz assay with potash, by a suitable admission of air at a lower temperature. By this process the K_2S of the sulpho-salt is completely converted into K_2SO_4, but the PbS only partly into $PbSO_4$, so that, by increasing the heat, the still remaining PbS is decomposed by the $PbSO_4$, as follows: ($PbS + PbSO_4 = 2Pb + 2SO_2$). In the first case, the presence of carbon (black flux, flour, tartaric acid, etc.) promotes desulphurization.

1. *Rich galena (with little earths).*

a. Assay in an iron pot (Belgian assay).—This is the best method of assaying lead, as pure galena with 86.6 Pb yields 84.25 to 85.25 per cent. of lead, therefore, with a loss of but 1 to 2 per cent. and sometimes only 0.5 per cent. of lead. It also permits the use of a larger charge, and, the iron pot being a good conductor of heat, the operation can be more quickly executed and at a comparatively low temperature. When large quantities of earth are present, more slag will be formed, and consequently the resulting loss of lead will increase, according to *Percy*,[1] at the following rate: 1.80 to 7.90 per cent. when the ore contains from 10 to 90 per cent. of calcium carbonate, and 1.18 to 35 per cent. when 10 to 90 per cent. of silicic acid is present. The sample is less frequently fused without any fluxes (Flintshire) than with alkaline fluxes. An addition of carbon (black flux, flour, argol) checks the oxidation of the lead, promotes the reduction of the lead carbonate and lead sulphate which may be present, and prevents the oxidation of the iron sulphide. The latter (oxide of iron) vigorously attacks the walls of the pot and retains particles of lead when the contents of the pot are poured out. Fluor-spar is a good flux for heavy spar. *Silver* and *gold* pass entirely into the lead, but only traces of *zinc* and *iron*. *Copper* divides itself between lead and slag. A large part of the *antimony* passes into the lead, and while a part of the arsenic volatilizes, very little of it passes into the lead and the largest part forms spiess with iron.

50 grammes (771.61 grains) of ore are placed in an iron pot previously heated to dark redness, in a coke fire in the wind furnace, or in a gas furnace. From 50 to 100 grammes (771.61 to 1543.23 grains) of black flux or potassium carbonate with 15 to 20 per cent. of flour are added, then 2 to 3 grammes (30.86 to 46.29 grains) of borax, and finally a covering of common salt 5 millimeters (0.197 inch) thick. The charged crucible is then placed between the darkly glowing coal in the furnace. The latter is closed, and the temperature *gradually* raised in about five minutes to complete redness, and this is kept up until the contents of the crucible are in quiet fusion without foaming (three to five minutes). The granules of lead floating on the top should be submerged

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[1] B. u. h. Ztg. 1871, p. 61.

by means of an iron spatula or wooden rod. The furnace is then closed for a few minutes, after which the pot is taken out and allowed to cool off somewhat. Its contents are poured into a mould, which should have been previously coated with graphite and heated. If the contents are poured out while too hot, a film of lead may remain adhering to the iron, and, if too cold, the lead will partly spread over the slag. The mould, after having been allowed to cool off, is turned over, and the hard, black slag is quickly broken off from the lead button to prevent it from becoming moist, as it would then not separate quite as well. The lead button is then washed with hot water or diluted sulphuric acid, dried, and weighed. The slag is again smelted with some potassium carbonate and flour or black flux for about 10 to 12 minutes, and then poured out. The time required for the fusion, counted from placing the ore into the pot to the first pouring out, is from 10 to 15 minutes. The iron pots will bear from 40 to 50 operations. In many works *lead matt* free from copper, poorer ores, and slag are assayed according to this method.

England[1] (Flintshire): 500 grains (32.4 grammes) of rich galena, 500 grains sodium carbonate, and 50 grains argol; for poorer ores: 350 grains of sodium carbonate, 150 grains borax, and 50 grains argol. The ore is mixed in a mixing scoop with a long spout (Fig. 6*a*, p. 32), with three-fourths to four-fifths of the quantity of the flux. The mixture is pushed to the front of the scoop, next to this the remainder of the flux is placed, and behind this the borax. The whole is then carefully poured into the dark glowing pot and subjected to the fusing operation mentioned above. In pouring out the contents the slag is kept back in the pot by means of a wooden rod, and is again fused with 20 to 30 grains of sodium carbonate and 5 to 10 grains of argol. The yield of lead from pure galena is generally from 84.25 to 85.25 per cent. The difference in the results of the assay is nearly the same for the richest ores and those yielding up to 50 per cent., but is greater in poorer ores. In *Wales* and *Flintshire* a yield of 75 to 82 per cent. Pb is obtained from pure galena by placing 10 ounces troy of the ore in a covered iron dish and fusing it in an open forge fire.—*Bleiberg* in *Carinthia:* 50 grammes (771.61 grains) of ore, 2 tablespoonfuls of flux (3 parts of argol, 2 saltpetre, 1 borax), a cover of powdered glass (or common salt), smelting for 12 to 15 minutes, etc.—*Belgium:* 10 grammes (154.32 grains) of galena with 28 grammes (432.10 grains) of sodium carbonate and 5 grammes (77.16 grains) borax, or 10 grammes (154.32 grains) sodium carbonate and 10 grammes (154.32 grains) argol.—*Tarnowitz:* 50 grammes (771.61 grains) of ore, with black flux, borax, and a covering of salt resting upon a layer of a little black flux. The difference between the separate assays is not more than 2 per cent.—*Mechernich:* 25 grammes (385.80 grains) of ore with 150 grammes (2314.8 grains) of borax and 100 grammes (1543.23 grains) sodium carbonate and argol in equal parts. For slag more borax, for lead matt more soda.

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[1] B. u. h. Ztg. 1862, p. 242; 1871, p. 61.

b. Assay with potassium cyanide in clay crucibles.—This can be executed at comparatively low temperatures, and gives a good yield, but is more expensive than the foregoing. Besides, the potassium cyanide is poisonous, and adheres to the porous mass of the crucible which may uncover the lead button and effect its oxidation.

The charge, according to *Levol*, is as follows: 100 parts galena, 100 potassium ferrocyanide, and 50 potassium cyanide with some sodium carbonate; according to *Ricketts:* 10 grammes (154.32 grains) of ore, 20 to 25 grammes (308.65 to 385.80 grains) of potassium cyanide, and a covering of common salt. The charge is fused for 12 to 15 minutes at a low temperature; the yield is 78.5 to 79.1 per cent. of lead.

2. *Galena with more earths.*

a. Assay with black flux (potassium carbonate and flour) and metallic iron, in clay crucibles.—When the ore contains large quantities of earth, more slag is formed. This, if the contents of the crucible were to be poured out, would retain considerable lead, which will settle if the charge is allowed to cool off in the crucible. The loss of lead is from 2 to 3 per cent. Deep crucibles (fig. 39, p. 66) are used for this purpose, and the charges fused in a muffle or wind furnace. The work can be done more conveniently in the latter, and fuel will also be saved. Should small quantities of metallic sulphides be present, it is well to roast the ore somewhat in a covered crucible to volatilize the arsenical sulphides, the sulphur from the iron pyrites, etc. Charge: 5 grammes (77.16 grains) of galena are placed on the bottom of the crucible, upon this is put a piece of iron wire 4 to 5 millimeters (0.157 to 0.196 inch) thick, and up to 9 millimeters (0.354 inch) long (it should be longer or shorter according to the percentage of lead, that is to say, about 25 to 30 per cent. of the weight of the ore). Upon this are placed 15 grammes (231.48 grains) of black flux (or potassium carbonate with 15 to 20 per cent. of flour) and, in case of basic gangues, 2 to 3 grammes (30.86 to 46.29 grains) of borax. Upon this comes a covering of common salt 5 millimeters (0.197 inch) thick, and on top of all a piece of charcoal the size of a hazel-nut, for maintaining a reducing atmosphere. The contents of the crucible are slowly heated in the *muffle* furnace until the yellow flame caused by the carbonization of the flour is no longer visible. The heat is then raised, and tongues of bluish flames arising from the carbonic oxide will make their appearance. The contents of the crucible should not froth too strongly, and for this reason the firing must be done very carefully, especially when low crucibles are used. When the "flaming" and frothing have ceased, the heat is still kept up for ½ to ¾ of an hour to allow the sulpho-salt (p. 86) to become decomposed by the metallic iron. 25 to 30 minutes are required for fusing the charge. The sample, fuming strongly from the vapors of the common salt, is then taken out, allowed to cool off, and freed from slag. By hammering the lead flat, the iron adhering to it will fly off. The lead button, which is covered with iron sulphide, is then brushed and weighed. The success of the assay is indicated by the iron still adhering to the lead without this being wrapped around it (to prevent this, the iron wire should not be too fine), by thoroughly fused slag and a malleable lead button. If brittle, it contains sulphur. The various assays must agree within 1 to 3 per cent. according to the richness of the ore.

Freiberg: 3.75 grammes (57.87 grains) of ore, 0.92 to 1.13 grammes (14.2 to 17.44 grains) of iron wire; 7.5 to 9.4 grammes (115.7 to 145 grains) of black flux or potassium carbonate with flour, 1.13 to 1.5 grammes (17.44 to 23.15 grains) of borax, and for basic gangue 2.25 to 2.63 grammes (34.73 to 40.6 grains) of glass, and a covering of common salt, 5 millimeters (0.196 inch) thick. The charge is heated from ¾ to 1 hour in the wind-furnace.—*Pribram:* 0.5 gramme (7.71 grains) of crude argol is placed in the bottom of the crucible, upon this iron wire, then 5 grammes (77.16 grains) of galena, and 12 grammes (185.1 grains) of black flux, and finally a covering of common salt. The charge is heated from 20 to 25 minutes in a gently glowing wind-furnace until the fusing mass subsides. The fire is then urged on, when the assay will emit gas (boil) vigorously, and, when this is the case, the firing is continued for 5 minutes longer. A difference of 2 per cent. is allowed in the assay of ores with 0 to 50 per cent. of Pb, and 3 per cent. in those with over 50 per cent.—*England:*[1] The same quantities of ore and flux are used as for assays in the iron pot (p. 87). The ore is placed in a Hessian crucible together with ¾ to ⅘ of the flux, and a strip of wrought iron in the shape of a horse-shoe is pushed into the mass. The crucible is gradually heated, requiring from 20 to 25 minutes, and during this time the iron is moved about several times. When the flux is thin fluid the crucible is taken from the furnace, the iron, which should be free from globules of lead, is removed, and the crucible allowed to cool. The contents is then poured out, and the lead button is freed from slag. If the heat has not been strong enough, the lead button will be hard, and will have a lustre like galena, and the slag will also be covered with a lustrous film. The yield of lead from pure galena is from 82 to 83 per cent. of Pb.—*New York:* 10 grammes (154.32 grains) of ore, 25 grammes (385.80 grains) of black flux, three loops of iron wire, which are taken out after the fusion is complete, and a covering of common salt. The yield from pure galena is 78.4 to 78.6 per cent., with a difference of 1 to 2 per cent. in the various assays.—*Upper Harz:* The assay was formerly conducted in the same manner as in *Freiberg*, but now iron pots are used.

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[1] B. u. h. Ztg. 1871, p. 62.

b. Upper Harz, assay with potassium carbonate.—A muffle-furnace is required for this method of assaying. Low crucibles (Fig. 39) may be used, as the charge contains no carbon, and several crucibles can be placed in the muffle at one time. The result of this assay is not as accurate, the yield being somewhat less than with the methods described above, as the success of the operation depends on the proper "*cooling of the assay*," for which there is no guide but experience. This method is therefore chiefly available for uniform ores only, the approximate yield of which is known. It has been almost abandoned at the present time.

Charge: 12.5 to 15 grammes (192.90 to 231.48 grains) of potassium carbonate are placed in a small crucible (Fig. 39, p. 66). To this is added 5 grammes (77.16 grains) of galena, and both are thoroughly stirred together with the mixing spatula. In case basic earths are present, 1 assay spoonful of borax is placed upon the mixture, and upon this a covering of common salt 5 millimeters (0.196 inch) thick. The charge is then placed in the thoroughly heated muffle-furnace, where it remains, with the mouth of the muffle closed, until it has come into perfect fusion (that is, when no more deposits are perceptible on the edges of the crucible). To decompose the sulpho-salt by oxidation, the mouth of the muffle is then opened for about 10 to 15 minutes, until the crucible appears dark and the vapors above it have greatly diminished or entirely disappeared (this is called *cooling the assay*). Thereupon the furnace is brought back to its first temperature, completely closing the muffle, in order to decompose the still remaining sulphurized lead by the sulphate which has been formed. The crucible is then taken out and allowed to cool off, and the lead buttons are freed from adhering slag. If the assay has been successful, the slag is completely fused, and the lead button has a pure lead color, but not much metallic lustre, as, if this is the case, the heat has been too strong.—For ore containing *antimony:* 10 grammes (154.32 grains) of ore, 35 grammes (540.13 grains) of potassium carbonate, 1 gramme (15.43 grains) of saltpetre, and a covering of common salt. 30 minutes are required for fusing, 10 minutes for cooling, and 10 minutes for the final heating of the assay.

3. *Galena containing large quantities of earths.*—The English method (p. 87) is employed with a strip of sheet-iron in the form of a horse-shoe, but stronger fluxes (caustic alkalies) are used, which, to be sure, attack the crucibles more energetically, and larger charges, as for instance: 100 grammes (1543.23 grains) of assay sample, 100 to 150 grammes (1543.23 to 2314.8 grains) of caustic soda, 150 to 250 grammes (2314.8 to 3858 grains) of potassium carbonate or sodium carbonate, strip of iron in the form of a horse-shoe 25 millimeters (0.098 inch) wide, and 4 millimeters (0.157 inch) thick. From 1 to 1½ hours are required for perfect fusion, and until the iron is free from lead globules.

B. Lead monosulphide with foreign metallic sulphides (galena with zinc blende, iron pyrites, etc.; lead matt, etc.).

1. *Roasting and reducing assay.*—The result of this assay is inaccurate, as the lead oxide is liable to slag off

and foreign metallic oxides to be reduced, the metal of which contaminates the lead. For this reason the assay with sulphuric acid is frequently used instead (*Rammelsberg* smelting works in the Lower Harz).

5 grammes (77.16 grains) of ore are roasted in a roasting dish. This is mixed in the assay vessel with 7.5 to 15 grammes (115.7 to 231.48 grains) of potassium carbonate and flour, or black flux. Upon this is placed 1.25 to 1.5 grammes (19.29 to 23.15 grains) of glass, then 0.25 to 0.5 gramme (3.85 to 7.71 grains) of thick iron wire, upon this 1.25 to 1.5 grammes (19.29 to 23.15 grains) of borax, then a covering of common salt, and on top of all a piece of coal. By fusing the roasted charge in the muffle- or wind-furnace at not too high a temperature, the lead oxide and lead sulphate are reduced (if the temperature is too high, many other metallic oxides are also reduced), and the foreign oxides and earths contained in the sample are slagged off by the aid of the potassium carbonate in the black flux, as well as of the borax and glass. The heating should be done with the greatest care, as the contents swell up very much. 20 to 30 minutes are required for smelting in the muffle-furnace after the "*flaming*" in the muffle has ceased, and from 15 to 20 minutes in the wind-furnace after the flames get under way.

Hungary: 10 grammes (154.32 grains) of roasted ore are charged with 11.5 grammes (177.44 grains) of black flux, and this is covered with a layer of 15 to 20 grammes (231.48 to 308.65 grains) of common salt. It is fused by keeping up a strong fire under the muffle for half an hour. The yield is from 10 to 12 per cent. Pb less than from an assay with metallic iron. It will be larger if charcoal dust is added in roasting, but the button will be less pure.

2. *Assay with sulphuric acid* (combined dry and wet method).—This gives more accurate results than the fore-

going processes, as the foreign metals are removed before fusion, but there will be always a loss of lead in the last-named operation.

5 to 10 grammes (77.16 to 154.32 grains) of the ore are ground as fine as possible. It is decomposed by digesting it with nitro-muriatic acid (*aqua regia*) in a glass flask with straight walls (Fig. 15, p. 42). A few drops of sulphuric acid are added, and it is then evaporated to dryness. The dry mass is digested with diluted sulphuric acid, filtered, and washed. The filter is freed from water between blotting-paper, and, with the residuum (lead sulphate and insoluble earths, clay, etc.), is dried in a roasting dish under the muffle, and finally incinerated at as low a temperature as possible. The mass is then ground up, and charged in a high crucible with 15 grammes (231.48 grains) of black flux (1 part saltpetre and 3 parts argol), and then with 1 to 1.5 grammes (15.43 to 23.15 grains) of iron. The charge is slowly heated, and then strongly heated after the "flaming" in the muffle has cased (15 to 20 minutes).—If the assay sample should contain *antimony*, which partly remains as lead antimoniate with the lead sulphate, the process is as follows: The assay sample is decomposed by nitric acid, to which some tartaric acid has been added. It is neutralized with sodium carbonate, and the antimony is extracted by digesting the mass for about half an hour in a solution of sodium sulphide containing sulphur. It is then filtered and washed, and the residuum is treated in the same manner as in the sulphuric acid assay.

II. *Oxidized Substances.*

A. Lead oxides free from earths (*litharge*, *minium*, *skimmings* (*Abstrich*) *etc.*).—5 grammes (77.16 grains) of the sample are fused at not too high a temperature with

12.5 to 15 grammes (192.90 to 231.48 grains) of potassium carbonate with 30 to 35 per cent. of flour, or black flux, and covering of common salt, with small pieces of coal on the top, in the same manner as in the roasting and reducing assay. If the sample should contain any sulphur, 0.25 to 0.5 gramme (3.85 to 7.71 grains) of iron wire are added. 20 to 25 minutes are required for fusion in the muffle-furnace after the "*flaming*" in the muffle, and 13 to 15 minutes in the wind-furnace after the flame is under way.

B. Lead oxides with earths.—The charge is the same as in II. A, with the exception that from 25 to 30 per cent. of borax are added, and 5 to 10 minutes more are required for fusion.

C. Salts of lead oxide, namely:—

1. *Lead carbonate* (*cerussite*), *lead chromate* (*crocoisite*), *lead phosphate* (*pyromorphite*), *mimetene* (*lead arsenate*), *and yellow lead ore* (*wulfenite*).—The charge is the same as in II. A, with an addition of from 20 to 30 per cent. of borax, according to the presence of more or less earthy substances. With pyromorphite containing arsenic from 5 to 10 per cent. of iron is added to separate the arsenide of iron. Time for fusion the same as in II. A.

Charges for oxidized ores according to *Percy:* 500 grains of ore, 350 grains of sodium carbonate, 150 grains, or less, of borax, and 50 grains of argol. The charge is fused in an iron pot (p. 87).—*Lead carbonate* (*cerussite*): 500 grains of ore, 500 grains of sodium carbonate, 100 grains of argol, and 30 grains of borax. The charge is fused for about 20 minutes in a clay crucible in the wind-furnace, and poured out (p. 91).—*Lead phosphate* (*pyromorphite*): 300 grains of ore, 400 grains of sodium carbonate, 20 grains of powdered charcoal, and 30 grains of borax; *or*, 350 grains of sodium carbonate, 100 grains of argol, 30 grains of borax, and some metallic iron. Fusing time: 25 to 30 minutes, counting from introducing the charge until it is poured out.

2. *Lead sulphate* (*anglesite, lead fume, dross, sweepings, tailings, skimmings, etc.*).—The charge is the same as for the assay with sulphuric acid (p. 95). If necessary a smaller quantity of metallic iron (for instance, only 10 per cent. for fume and skimmings which carry but little sulphate) is used, and 20 to 30 per cent. of borax is added if earths are present.

3. *Lead silicate* (*slags*).—10 grammes (154.32 grains) of slag are ground as fine as possible, and mixed in an assay vessel with 15 grammes (231.48 grains) of potassium carbonate with 30 to 35 per cent. of flour. Upon this, in case of acid slags, are placed 1 to 2 grammes (15.43 to 30.86 grains) of borax. For basic slags, 2.5 to 5 grammes (38.58 to 77.16 grains) of borax, or equal parts of glass and borax, are taken, and for slag containing sulphur, and which may not have been previously roasted, 0.25 to 0.5 gramme (3.85 to 7.71 grains) of iron and a covering of salt with a piece of coal. The charge is smelted in a tall crucible (Fig. 39, p. 66), such as is used in the roasting or reducing assay, or in the crucible shown in Fig. 42, p. 67. 1 to 1½ hours are required for smelting acid slags in the muffle-furnace, and ¾ to 1 hour for basic slags in the wind-furnace after the flame is free. A thin liquid fusion is absolutely necessary, so that the lead globules can unite, this being the reason why a longer smelting is required.

III. *Alloys of Lead.*

The wet method must be employed for assaying alloys of lead.[1]

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[1] Analysirmethoden für Blei; Fresenius' Ztschr. viii. 118 (Fresenius); Preuss. Ztschr. x. 125 (Hampe).

26. WET ASSAYS.

These, if accurate results are to be obtained, require much time, and, as a necessary conditi the absence of certain substances. These pr semble the manipulations occurring in chemica and for this reason we will give here only proces can be easily carried out.

A. Assay by gravimetric analysis.

1. *Assays in Bleiberg in Carinthia and other* —2 grammes (30.86 grains) of galena are powd fine as possible and heated with nitric acid. Wh vapors cease to come off, the mass is evaporated ne dryness with a few drops of sulphuric acid. If much is present, it is diluted with $\frac{1}{8}$ of a liter (0.2 pint) of before the sulphuric acid is added, and the evapora with the nitric acid is not carried too far in order to k as much as possible of the lime in solution. It is th allowed to cool off, diluted, filtered, and washed until acid reaction of the wash-water ceases. The contents the filter (lead sulphate and insoluble earths, sulphu etc.) are then rinsed off into a beaker glass, and digeste with a concentrated solution of neutral sodium carbonate to convert the lead sulphate into carbonate. It is then filtered and washed until the water does not become clouded by the addition of barium chloride. The residuum is heated with diluted nitric or acetic acid to extract the lead, filtered, and the filter is washed with hot water until acid reaction ceases. The lead is then precipitated from the filtrate with as small a quantity of sulphuric acid as possible, to prevent a precipitation of lime with it. The lead sulphate is filtered, washed with

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[1] B. u. h. Ztg. 1871, p. 62.

hot water, and dried. It is then detached from the filter, heated to a red heat, and weighed. There should be at the utmost a difference of 0.1 per cent. between assay and counter-assay.—Another process is as follows: The ore is dissolved in nitro-muriatic acid (*aqua regia*) and evaporated to dryness. The lead chloride (as also the ferric chloride and copper chloride) is extracted by boiling water and filtered. The filtrate is neutralized with ammonia to the precipitating point. The lead is precipitated with diluted sulphuric acid, and allowed to stand quietly for 6 hours. The lead sulphate is then filtered and washed, the filter dried and burned, and the sulphate heated and weighed.

2. *Mohr's process.*—1 gramme (15.43 grains) of finely powdered galena is boiled in a glass or porcelain vessel with hydrochloric acid. To this is added a small piece of zinc, and the contents of the vessel is then heated until the fluid becomes clear. The precipitated lead is washed by decantation and dissolved in diluted nitric acid. It is then filtered to free it from adhering insoluble substances (quartz, heavy spar, etc.). The filtrate is very much diluted with water, and the lead is precipitated as lead sulphate with sulphuric acid in the same manner as in 1.

Storer[1] weighs the lead precipitated with zinc, directly, or dissolves it, in case it contains insoluble admixtures, in nitric acid, then weighs the residue and obtains the weight of the lead from the difference. Mascazzini[2] fuses the impure lead, which has been dried, with a mixture of 1½ to 2 parts of caustic alkali, 5 parts of borax, and 5 parts of starch. Löwe[3] frees the lead sulphate from its admixtures with earths by dissolving it in sodium hyposulphite, precipitates it as sulphide with sulphuretted hydrogen, and converts this into sulphate. Riche[1] determines the lead as superoxide by electrolysis. The galena is dissolved in hydrochloric acid. The clear solution is filtered into diluted sulphuric acid, and the lead determined as sulphate. But this must be ignited gently to prevent the volatilization of traces of lead chloride which may be present, as this would make the result less accurate.

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[1] Storer, in Fresenius' Ztschr., ix. 514; B. u. h. Ztg. 1870, p. 208; 1873, p. 91.

[2] Mascazzini, in Dingler, ccvii. 46; B. u. h. Ztg. 1878, p. 382.

[3] B. u. h. Ztg. 1874, p. 322.

B. Volumetric processes.[2] — These have been frequently proposed without any practical success.

C. Colorimetric processes. — Bischof[3] has given a method for determining small quantities of lead, which is based upon the browning of a solution containing lead, by sulphuretted hydrogen.

II. COPPER.

27. ORES.

Native copper. — Sulphuretted ores: *copper glance*, Cu_2S, with 79.7 Cu; *erubescite* (*purple copper ore*), Cu_3FeS_3, with 55.6 Cu; *copper pyrites*, $CuFeS_2$, with 34.6 Cu. Ores with antimony or arsenic: *tetrahedrite* (*Fahlerz*), $R_4Q_2S_7$ (in which $R = Cu_2$, Ag_2, Fe, Zn, Hg, etc., $Q = Sb$, As), with 15 to 48 Cu, as much as 30 per cent. silver, and from 0 to 18 per cent. mercury; *bournonite*, $PbCuSbS_3$, with 13.03 Cu and 42.54 Pb; *enargite*, Cu_3AsS_4, with 48.6 Cu. Oxidized copper ores: *cuprite* (*red copper*), Cu_2O, with 88.8 Cu; *malachite*, $CuCO_4 + H_2O$, with 58 Cu; *azurite*, $Cu_3C_2O_7 + H_2O$, with 55.2 Cu; *dioptase* (Kieselmalachit), $CuSiO_3 + 2H_2O$, with 35.7 Cu; *atacamite*, $Cu_4O_3Cl_2 + 3H_2O$, with 59.4 Cu; *phosphates of*

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[1] B. u. h. Ztg. 1878, 382.

[2] Mohr, Lehrbuch der Titrirmethode, 1874, p. 460; Fleischer, Titrirmethode, 1876, pp. 42, 87, 293; Mitchell, Practical Assaying, 1868, p. 397.

[3] Fresenius' Ztschr. 1879, p. 43; B. u. h. Ztg. 1879, p. 187.

copper, with 30 to 56 Cu; *arsenates of copper*, with 25 to 50 Cu; *cupric sulphate* or *blue vitriol*, $CuSO_4+5H_2O$, with 25.3 Cu.

28. DRY ASSAYS.[1]

These, besides consuming much time, and being expensive, require great experience and are less accurate than the wet assays, which are now much employed in smelting works for valuing ores. There are two methods, known as the *German* and the *Cornish* assay. Both are based upon the principle that copper has a stronger affinity for sulphur, and less for oxygen, than the foreign metals (iron, zinc, antimony, lead, arsenic, etc.) with which the ores are contaminated, so that, when they are present in an oxidized condition, or have been converted into it by roasting, they are mostly slagged off at comparatively low temperatures on being fused (*reducing fusion*) with reducing agents (black flux free from sulphur, potassium carbonate and flour) and solvent agents (borax, glass), and only a very small part of them passes into the reduced copper (black copper). The latter during the subsequent oxidizing fusion (*refining*) eliminates the foreign metals in an oxidized condition, and is itself transformed into refined copper, while the metallic oxides which have been formed are either slagged off by the solvent agent (borax) or are carried into the cupel by the lead oxide. On account of the difficult fusibility of copper, it is well to add in the reducing fusion *collecting* and *liquefying* agents (such as antimony and arsenic, but lead is less well adapted as it may cause losses in the refining). The *German* and *Cornish* or *English* methods, which undergo modifications accordingly as the copper is combined with sulphur, antimony, or arsenic, or is oxidized or alloyed, are still practised in smelting works, and give results which suffice for the business of working copper on a large scale.

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[1] B. u. h. Ztg. 1867, p. 105.

A. *German copper assay.*

1. *Ores with sulphur, antimony, or arsenic.*

a. Roasting.—Dead roasting 5 grammes (77.16 grains) of ore, or enough of it is dead roasted that the refined button of copper, to be turned out on the refining dish, does not weigh much over 0.5 gramme (7.71 grains). It is then repeatedly rubbed up and treated with coal and finally with ammonium carbonate for completely removing the sulphur (p. 35) which otherwise would produce copper sulphide and occasion losses during reducing fusion. A well-roasted sample should be earthy (without metallic lustre), have a brownish or black color, should not appear sintered, and should neither fume nor smell.

Pyrites is rubbed up two or three times and treated once with powdered charcoal.—Tetrahedrite, *Fahlerz* (Hungary): 10 grammes (154.32 grains) of ore are rubbed up ten to twelve times at a very low roasting temperature, taking them out whenever they commence to fume. The ore is then roasted without charcoal for $\frac{3}{4}$ to 1 hour at a temperature not above red heat, rubbed up, and roasted for 1 hour more at a white heat.

b. Reducing and solvent fusion.—The roasted ore is well mixed in an iron mortar with $\frac{1}{3}$ of the required quantity of black flux (consisting of 2 to $2\frac{1}{2}$ parts of argol and 1 part of saltpetre, or of 3 parts of potassium carbonate and 1 part of flour), a collecting agent (antimony is the best) and, if the ore contains no iron, some iron filings are added to decrease the slagging of copper in refining it on the dish. The mixture is poured by means of the mixing scoop (Fig. 6, p. 32) into a suitable crucible of refractory clay (Fig. 42, p. 67). The remaining $\frac{2}{3}$ of the flux is then added, upon this is placed a mixture of borax and glass, then a covering of common salt and a small piece of charcoal.

Examples of Charges.

	Black flux.	Borax.	Glass.	Antimony (arsenic).	Iron filings.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Pyrites (copper)	300	50	40	10	
Purple copper ore	300	40	40	10	
Tetrahedrite	300	30	25	6	8
Matt rich in iron	300	40 to 50	40	10	
Matt rich in copper . . .	300	....	50 to 100	5	

Charges suitable in many cases: 5 grammes (77.16 grains) of ore, 12.5 to 15 grammes (192.90 to 231.48 grains) of black flux, 0.3 gramme (4.63 grains) of antimony, 1.25 grammes (19.29 grains, 1 small assay spoonful) of borax, 1.5 to 2.5 grammes (23.15 to 38.58 grains) of glass, and 10 to 15 grammes (154.32 to 231.48 grains) of common salt; or 5 grammes (77.16 grains) of roasted ore are mixed with the same quantity of black flux and put into the crucible. Upon this are placed 8 to 10 grammes (123.46 to 154.32 grains) of black flux, 1 gramme (15.43 grains) of borax, 2.5 grammes (38.58 grains) of glass, and a covering of common salt 6 millimeters (0.236 inch) thick. *Hungarian fahlerz:* Half of the roasted sample = 5 grammes (77.16 grains) is mixed with 7 to 8 grammes (108.02 to 123.5 grains) of black flux. The mixture is placed upon the same quantity of black flux in the crucible and covered with common salt.

American charge: 10 grammes (154.32 grains) of ore are roasted and mixed with 20 grammes (308.64 grains) of black flux, 3 grammes (46.29 grains) of borax glass, and 10 to 20 grammes (154.32 to 308.64 grains) of hematite. Upon this are placed 10 grammes (154.32 grains) of black flux, 3 grammes (46.29 grains) of wood charcoal, and a covering of common salt. Charge for unroasted ores containing heavy spar and gypsum: 5 grammes (77.16 grains) of ore, 5 grammes of borax glass, 5 grammes of powdered glass, and 10 per cent. of rosin; and, besides for poor ores, 25 per cent. of iron pyrites if this is not already present in the ore. The whole is covered with common salt and fused to matt, which is then roasted and treated as above.

Time required for fusion: $\frac{3}{4}$ to 1 hour in a red heat in the muffle-furnace after the "flaming" has ceased, or in a wind-furnace after the flames are free. The charcoal should be piled high in front of the crucibles in the muffle. Indications of a successful assay are: a well-fused regulus (which, on account of its brittleness, must be carefully freed from slag), without a black coating of brittle matt rich in copper, well-fused slag, whose color may be black or green, but must not be red, and without an admixture of metallic grains.

c. Refining.—This consists in an oxidizing fusion, during which the foreign metallic oxides are sooner oxidized than the copper, and are easily separated, either at once as easily fusible masses, though this is seldom the case, or must be dissolved by fluxes (borax, lead oxide), and then separate with these as slag (refining with borax on the refining-dish), or are absorbed by the cupel (refining with lead).

Lead is pre-eminently oxidizable. The lead oxide yields its oxygen to the foreign metals. It therefore acts as a vigorous oxidizing agent, and produces easily fusible combinations, but it contributes to the slagging off of the copper, and for this reason the refining process with lead is less accurate than that with borax without lead. *Ferrous oxide*, *antimony*, and *arsenic* protect copper from slagging. *Nickel* and *cobalt* are difficult to separate from copper, and do so only at the expense of considerable copper which is slagged off (see assay of nickel). *Tin* and *zinc* give refractory oxides and slags, and, if present in large quantities, the wet method must be employed. Gold and silver remain in the refined copper.

α. Refining on the dish. a. *With borax.*—This is the most accurate process (to within 1 to ½ per cent.), and is principally adapted for black copper free from lead, or which contains iron, arsenic, or antimony. According to the size and impurity of the copper button, 1.25 to 2.5 grammes (19.29 to 38.58 grains) of borax glass are placed, either wrapped up in a cornet, or by means of an iron spoon, in a refining-dish, which stands in the white-hot muffle, and is surrounded by glowing coals. The copper button, weighing from 0.5 to 0.6 gramme (7.71 to 9.26 grains), is taken up with the curved tongs (Fig. 39, p. 66) and placed into the dish. The mouth of the muffle is then closed by a plug, or by piling coal in front of it, and the button is fused quickly at as high a temperature as possible. The mouth of the muffle is then slightly opened to allow an access of air. On account of the oxidation of the foreign metals (iron, zinc, etc.), the button will at first appear dull, but brightens as soon as the foreign metals (with the exception of antimony and arsenic) have been removed, and fumes from the antimony or arsenic, which may have been originally present, or has been added as a collecting agent. (The first fumes more strongly than the latter, therefore indicating the end of the process more plainly.) The completion of the refining process may be recognized by the button, which *remains bright*, ceasing to fume (should the process be continued the button would become dull from a covering of cuprous oxide); and also, by the subsiding of the slag, that is, if the button is not too large, and does not weigh much over 0.4 to 0.5 gramme (6.17 to 7.71 grains). The dish is then taken out with the curved tongs (Fig. 46*b*, p. 74), and carefully cooled off *upon* water until it ceases to glow, and then *in* water, and the button freed from slag. The assay is considered successful if the button on being flattened shows itself ductile to a certain extent, and has a flesh-red color exteriorly. (A small residue of antimony and arsenic prevents the button from being entirely ductile, and causes its fracture to be gray, and equalizes small losses in slagging off.) The slag should not be red, or at least scarcely perceptibly so, except at the place where the button has lain. Red slag indicates, either that the oxidizing process has been carried too far, or an absence of iron which otherwise protects the copper from slagging off during the reducing fusion, as well as during refining.

b. *By itself, without borax and lead* (*Hungarian speiss assay*[1]) for buttons containing more antimony or lead.—The copper button is placed on the white-hot refining-dish (p. 66) standing in the muffle, and is fused quickly at as high a temperature as possible after the mouth of the muffle has been closed. After the fusion is complete the mouth of the muffle is opened, the register closed, and the dish turned and lifted. This will cause the slag formed from foreign oxides to remain behind, and the button to roll upon a place free from slag. The refining is continued in this manner until the fuming ceases, and the now refined button assumes a sea-green color. The refining-dish is then pulled slowly towards the mouth of the muffle, and taken out as soon as the button brightens. The dish is then dipped in hot water, when the button can be hammered out without cracking on the edges. It should have a red color. It is now weighed, and the difference in weight between it and the black copper determined. From this the loss of copper, which must be placed to the account of the copper, is calculated by allowing for plumbiferous copper 1 part for every 10 parts of black copper lost, and for antimonial and arsenical copper 2 parts for every 10 parts lost.

If the ore should contain neither lead, antimony, nor arsenic, a little borax is added, and some lead during the fusing process should the copper be very refractory, for instance, if it contains much iron, or cobalt and nickel.

c. *With lead and borax* (*Müsen assay*).—The black copper obtained from 5 grammes (77.16 grains) of ore is fused with 2.5 grammes (38.58 grains) of granulated lead and a small quantity of borax. The muffle is slightly opened to give access to the air until the copper brightens in the continually increasing brownish slag. The dish is cooled off in water. A counter-assay with refined copper is made, and the loss of copper occurring thereby is added to the principal assay. 10 parts of lead will slag off about 1 part of copper.—*In Mansfeld*, 2.5 grammes of black copper were formerly refined with 0.4 gramme of lead.

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[1] B. u. h. Ztg. 1866, No. 28; 1868, No. 12; 1871, p. 255.

β. Refining by cupellation.—This method is the most suitable one for plumbiferous black copper, and especially for quickly obtaining approximate results. But a correction (*counter-assay*) is necessary to determine the amount of copper slagged off by the lead which becomes oxidized during the oxidizing fusion, and then parts with oxygen, not only to the foreign metals, carrying them with it into the cupel, but also slags off a part of the copper.—A quantity of refined copper, equal to the weight of the black copper button—for instance, 1 to 1.25 grammes (15.43 to 19.29 grains)—is weighed off for the counter-assay. The assay sample and the counter-assay sample are each wrapped up in a cornet. A quantity of granulated lead, amounting to 2 or 2½ times the quantity of copper, is weighed off for each copper sample, and each also wrapped up in a cornet. Two large-sized cupels (Fig. 44, p. 68) are placed along-side each other in the centre of the strongly heated muffle, and are brought to a white heat. Upon each is placed one cornet with lead, and the mouth of the muffle is closed until the lead has begun to "*drive*" (that is until the dark film of lead has disappeared, and a white strongly fuming surface has made its appearance). The muffle is then opened, the cornet containing the refined copper is placed in one cupel, and that containing the black copper in the other, whereupon the muffle is again closed, and "driving" is quickly renewed at a high temperature. The mouth of the muffle is then slightly opened to admit air for the oxidation of the lead and the foreign metals, the oxides of which are absorbed by the cupels, until the copper buttons brighten. As soon as this has ensued a spoonful of coal-dust is strewed upon the cupels to prevent the slagging off of copper. They are then immediately taken out of the furnace and thrown into water. Both buttons are weighed, and the loss of weight of refined copper is added to the weight of the refined button obtained from the black copper.

γ. *Refining with the blowpipe.*—2.5 grammes (38.58 grains) of ore are roasted, arsenized, and fused as in the nickel assay (see § 40). The button is weighed, and 0.05 to 0.1 gramme (0.77 to 1.54 grain) of it is taken and fused with borax glass upon charcoal in the inner flame of the blowpipe. The oxidizing flame is then used until the dull button has become bright; it is then further treated upon charcoal without borax in the reducing flame before the blowpipe until it ceases to fume. The bright copper button is weighed, and the weight calculated to the quantity of ore used (*Rothenbach* smelting works near Müsen).

2. *Oxidized substances without sulphur.*—These are fused to black copper (p. 101) without being roasted, and the black copper is refined (p. 104), during which a percentage of iron will protect the copper from slagging.

	Black flux.	Antimony (arsenic).	Borax.	Glass.	Charcoal dust.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Poor ores with basic gangue	300	10	30 to 40	20 to 25	
" " acid "	300	10	60	15	
" " basic & acid "	300	12	30	30	
Richer ores	300	5 to 10	30 to 40	30 to 40	
Very rich ores	300	5 to 10	30 to 40	30 to 40	5 to 10
Rich slags	300	5	30	30	5 to 10
Poor slags	300	25 to 50	30 to 50	15 to 20	

From 1 to 10 per cent. of iron filings may be added for refining in case the copper contains no iron or other easily oxidizable metals.—The process of fusing *very poor copper ores* in larger quantities is as follows: 10 to 15 grammes (154.32 to 231.48 grains) of unroasted ore are mixed with 15 to 20 per cent. of iron pyrites (free from copper), and 20 per cent. of sulphur, 100 per cent. of borax glass, 100 per cent. of glass, and 20 to 25 per cent. of resin are added, and a covering of common salt. The charge is then fused to matt (matt assay) in a clay crucible. The resulting matt is roasted, etc.—Easily decomposable sulphates (cupric sulphate) are decomposed, before they are subjected to the reducing fusion, by roasting with an addition of charcoal (p. 35); sulphates difficult to decompose (cuprous sulphate with calcium and barium sulphates) by preliminary fusion to matt.

3. *Alloys of copper.*—In case they do not contain too many and difficultly oxidizable components (nickel, tin, etc.), they are refined in the refining-dish or cupel; otherwise the wet method of treatment is preferable.

B. Cornish copper assay.[1]—This is an imitation of the English smelting process in the reverberatory furnace, and requires much skill. On account of its inaccurate results (involving a loss of from 20 to 40 per cent. of copper, according to the richness of the ore) the wet method has been substituted for it even in Cornish smelting works for valuing ore in quantity. The following operations are required for ores containing sulphur, antimony, or arsenic: A gentle roasting in a suitable crucible (Fig. 40, p. 66);

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[1] Mitchell, Manual of Practical Assaying, p. 299.

fusing to crude matt in the same crucible. This is then roasted, and the roasted assay sample is fused to black copper. This is purified by fusing it with oxidizing and solvent agents, and the purified black copper is refined with oxidizing and solvent agents, and, finally, the slag is fused. All operations are carried out in the Cornish clay crucibles (Fig. 40, p. 66).

29. WET ASSAYS.

These, on account of their greater accuracy and simpler execution, have, as a general rule, been substituted for dry assays. The choice of one of the numerous wet assays depends chiefly on the foreign admixtures (antimony, arsenic, lead, bismuth, mercury, etc.), and somewhat on the richness of the sample. *Colorimetric* assays are especially adapted for poorer ores, and *volumetric assays*, if many are to be made in quick succession, are preferred to *gravimetric assays*.

A. Gravimetric assay.—The methods by which the copper is determined in the metallic state (Swedish and electrolytic assay) are simpler and more convenient to execute than those by which the copper is separated and determined in combination (determination of copper as cuprous sulphide, or as subsulphocyanide). The Swedish assay can be executed in less time than the electrolytic assay, but it is done at the expence of accuracy, especially with poorer ores.

1. *Modified Swedish assay.*[1]—The cupriferous substance is brought into solution with sulphuric or hydrochloric acid (nitric acid must not be used, as the precipitated copper is again dissolved in it), and the copper precipi-

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[1] B. u. h. Ztg. 1869, p. 12.

tated with *iron* or *zinc*, and determined either as metal or oxide. This plan is not admissible in the presence of metals, which are also precipitated by iron and zinc.

But such metals can be removed during the operation without injurious effect (*lead* as sulphate, *silver* as silver chloride, mercury by igniting the precipitated copper); or they must be removed by a preparatory operation (*arsenic* by roasting the assay sample with charcoal powder, or first by itself, and then with an addition of some iron pyrites at not too high a temperature; *tin* and *antimony* by heating with moderately diluted sulphuric acid, then adding nitric acid, and heating nearly to boiling, and an addition, if necessary, as in the case of metallic sulphides, of a few drops of fuming nitric acid. The solution is then evaporated to dryness until the fuming ceases. The dry mass is dissolved in hot water and filtered, and the solution treated with some hydrochloric or nitric acid, etc.; *or*, the antimony is removed by fusing the assay sample with potassium hydrate or potassium carbonate in a silver crucible, lixiviating the potassium antimoniate, and dissolving the residue; *or*, the assay sample is dissolved, neutralized with soda, and digested with a solution of sodium sulphide to extract the antimony, arsenic, and tin in soluble form. It is now filtered, and the residue washed and dissolved as above. To separate *bismuth* by analytical methods is a very tedious operation.—Ores containing *bitumen*, for instance cupriferous schists (Kupferschiefer), must be ignited to remove the bitumen, before they are dissolved. Impure (black) precipitated copper can be further examined according to *Parkes'* and *Fleitmann's* volumetric method, to be shortly described.

a. Precipitation with iron.—1 to 5 grammes (15.43 to 77.16 grains), according to degree of richness of copper; generally, 2.5 to 5 grammes (38.58 to 77.16 grains) of the assay sample are decomposed in a suitable flask (Fig. 9, p. 38), which is placed in an oblique position, by heating with sulphuric acid, and adding from time to time some fuming nitric acid, or potassium chlorate, until the separated sulphur, inclosing particles of the ore, is oxidized as much as possible; or, the sample is at once dissolved in *aqua regia* (see also p. 39 for method of decomposing metallic sulphides). It is now evaporated to dryness with some sulphuric acid, or until the sulphuric acid vapors appear in the flask. A few drops of sulphuric acid are added to the dry mass (to dissolve the basic salts), and then water is cautiously added; or, is at once added to the (cooled off) mass, while it still contains free acid. The fluid now *entirely free from nitric acid* is filtered into a glass flask, such as is shown in Fig. 15, p. 42. The residue is washed until the wash-water no longer produces a red stain upon a piece of bright sheet iron. Two pieces of iron wire, 3 to 4 centimeters (1.18 to 1.57 inches) long, are then added (or, in order to shorten the time required for the assay, the fluid may at once be filtered into a porcelain dish in which the iron wires lie, and copper will then be precipitated during the filtration). The filtrate is sufficiently diluted and gently heated until a pointed iron wire, when dipped into the fluid, shows no reddish stain of copper. The copper is twice decanted with *cold* water in a spacious beaker-glass (to prevent the separation of basic iron salts, which are more easily formed by hot water), and is then decanted three times with boiling water. The flask is now completely filled with cold water; a flat-bottomed porcelain dish, about 80 millimeters (3.15 inches) wide and 20 millimeters (0.78 inch) high, is placed bottom upwards on top of it. The flask and dish are then inverted. The mouth of the flask is held in an oblique position, and the water is allowed to run into the dish until it is nearly full. The flask is left standing in the dish until all the copper and the iron wires have fallen into the water in the dish (small particles of carbon separated from the iron will remain floating on the water for some time). The flask is now quietly drawn over the side of the dish, which should be somewhat inclined for the purpose. The iron is freed from copper by rubbing with the fingers, which should be rinsed off in the water. The copper is now decanted twice with boiling water. This is poured off as completely as possible from the copper, which is moistened with absolute alcohol, and dried on the water-bath, until it has assumed a pulverulent condition. It is allowed to cool in the desiccator, and is then brought upon the pan of the balance, or into a tared porcelain crucible with the aid of a fine brush, and quickly weighed. It is now dried for 10 or 15 minutes more, and again weighed until the results agree; or the copper is spread out upon a roasting dish and ignited in the muffle-furnace, and the metal calculated from the amount of cupric oxide formed (100 cupric oxide = 79.88 copper). If the water used in decantation shows a reddish sediment in the beaker-glass it should be filtered, the filter dried and ignited upon the scorifier, and the percentage of copper resulting from the cupric oxide should be added to the principal yield.

Correction for *iron* that may be contained in the precipitated copper on account of a deposit of basic iron salts: The precipitated copper is ignited upon the scorifier until it becomes black. The cupric and ferric oxides formed are weighed and dissolved in hydrochloric or sulphuric acid. The ferric oxide is precipitated with ammonia. The solution is filtered upon a small filter of paper. The filter is dried and ignited, and the ferric oxide, which may be found, is deducted from the combined weight of the cupric and ferric oxides, and the copper calculated from the quantity of pure cupric oxide found. Instead of decanting the precipitated copper, it may all be filtered, dried, ignited, weighed, and dissolved, as above, for obtaining the percentage of iron.

Pure precipitated copper has a fine copper color. If the solution contains antimony and arsenic, it has first a copper color, which changes to black, by the antimony and arsenic which are precipitated later on. The largest portion of the antimony, after the precipitate has been evaporated to dryness with sulphuric acid and again moistened with water, remains as basic sulphate of antimony, while arsenic passes into solution. The residue from the solution of the ore, etc., is tested for copper by heating it with nitric acid, filtering, and adding ammonia in excess (appearance of a blue color indicates copper).

Instead of two iron wires, a simple one, bent into the form of a ring with one end projecting vertically, may be used. The ring is dipped into the liquid contained in a beaker-glass in such a manner that the end projects. When the precipitation is complete the copper is rinsed from the ring, decanted, etc., as above.—Or a strip of sheet-iron may be used instead of the wire, but it must be immediately removed from the liquid after the precipitation of the copper is complete to avoid the formation of basic iron salts. In solutions that are too concentrated the copper adheres too strongly to the iron.

b. Precipitation with zinc free from lead and arsenic.[1]—A solution of the assay sample is prepared with sulphuric acid, as described on p. 112, and filtered. A strip of zinc is placed in it, and the solution is then heated until a bright iron wire held into it shows no copper deposit; or until a drop of the solution placed upon a porcelain dish is not browned by sulphuretted hydrogen. The strip of zinc is then taken out, and the precipitated copper is washed off with the wash-bottle. It is filtered, until but a small layer of water covering the copper remains. A few drops of warm hydrochloric acid are then added to dissolve any particles of zinc which may be present. It is now decanted, etc., as in the precipitation with iron (p. 113); or it is filtered as soon as effervescence has ceased, quickly washed with hot water, and dried. The copper is then detached from the filter, ignited on the cover of a porcelain or platinum crucible, or upon a roasting dish in the muffle, and the oxide quickly weighed. The black crust upon the end of the piece of zinc, which has been dipped into fluid, is a spongy layer of zinc colored by a trace of sulphide of copper. *Nickel*, which is not thrown down by iron, is precipitated with zinc, but cobalt is not.

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[1] Fresenius' Ztschr. für analyt. Chemie iii. 334 (Mohr und Fresenius). Oest. Ztschr. 1868, No. 48 (von Kripp). Erdmann's J. f. pr. Chemie, cii. 477 (Ullgreen). Darstellung von pulverförmigem Zinke in Dingler, ccxxviii. 378.

Granulated zinc may be used instead of a strip, but the granules must be completely dissolved by the time the bubbles cease. The copper is then decanted, etc.—The cuprous fluid may be filtered into a platinum dish, and some hydrochloric acid added to it. It is then heated, and a few small pieces of zinc added to it, whereupon the copper will deposit itself firmly on the platinum, but loosely on the zinc. After precipitation is complete, which fact is to be tested with sulphuretted hydrogen, as above, the copper is rubbed and washed off from the zinc. It is then allowed to settle, is decanted, treated with hot water, to which some hydrochloric acid has been added; then quickly washed with hot water by decantation to prevent the loss of any of the copper by solution. It is finally moistened with some absolute alcohol, dried in a water-bath, or at 110° to 120° C. (230° to 248° Fahr.), and the tared platinum dish, which has been allowed to cool off in the desiccator, is weighed; or the copper, if the utmost accuracy is demanded, is heated in a stream of sulphuretted hydrogen. —*Cuprous schist* (Kupferschiefer):[1] 5 grammes (77.16 grains) are heated with 40 to 50 cubic centimeters (2.44 to 3.05 cubic inches) of hydrochloric acid. When the carbonic acid has been expelled, 6 cubic centimeters (0.36 cubic inch) of diluted acid, consisting of equal parts of nitric acid, of 1.2 specific gravity, and water, are added (to ores free from bitumen, or which have been ignited, 1 cubic centimeter (0.061 cubic inch) of nitric acid). This is digested for half an hour, then boiled for a quarter of an hour. The hot liquid, which should contain no free nitric acid, is filtered into a beaker-glass. A small rod of zinc upon a strip of platinum is placed in the filtrate, and the copper is precipitated, which will require from ½ to ¾ of an hour. The precipitated copper is then decanted and dissolved in nitric acid, together with that adhering to the platinum, and titrated with a solution of potassium cyanide (see p. 127).

2. *Electrolytic assay.*[2]—The copper is precipitated in a coherent film upon a weighed platinum strip by the

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[1] Fresenius' Ztschr. viii. 9.

[2] Fresenius' Ztschr. iii. 334; vii. 253; ix. 102. B. u. h. Ztg. 1869, p. 43, 181; 1872, p. 251; 1875, p. 155; 1877, p. 5, 32. Preuss. Ztschr. xvii. Lief. 3; xx. Lief. 1. Grothe, polyt. Ztschr. 1877, p. 11.

galvanic current, from the solution of the nitrate containing free nitric acid, which need not be filtered. From this solution, *zinc*, *iron*, *nickel*, *cobalt*, and *chromium* are *not* precipitated by galvanic action. The following are precipitated in the form of peroxides at the positive electrode: namely, *lead*, *manganese*, and (partially) *silver*. *Mercury* is precipitated at the negative electrode in the metallic state before copper; *silver* and *bismuth* at the same time as copper, and *selenium*, *antimony*, and *arsenic* only a considerable time later; the assay, therefore, as a general rule, requires the absence of the last-named metals and metalloids, which blacken the fine red color of the copper. Antimony remains behind, undissolved, when the assay sample is dissolved in nitric acid. A large number of assays can be carried out at the same time according to this very accurate and simple method, which is adapted for rich as well as for poor ores, etc.

It is best to employ for the galvanic current, the *Meidinger-Pinkus' battery*[1] (with 6 large elements for richer copper ores, and 4 small elements for poor ores with less than 10 per cent. Cu); or *Clamond's thermo-electric battery*[2] (consisting of a number of zinc and antimony elements arranged in the form of a ring, and heated by a gas-flame) may be used. If the current is too strong the copper does not deposit itself firmly upon the platinum. The copper is not precipitated in as pure and coherent a state, from the solution of the sulphate containing free sulphuric acid, and in case iron should be present a part of this is thrown down with the copper, while another part is reduced to protoxide.

1 gramme (15.43 grains) of the assay sample is dis-

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[1] Fresenius' Ztschr. xi. 4 (Mansfeld).

[2] B. u. h. Ztg. 1875, pp. 155, 251, 303.

solved in strong nitric acid and evaporated to dryness in a porcelain dish. If necessary, the dish is heated over a lamp to burn off any separated sulphur (p. 39). The residuum is dissolved in 20 cubic centimeters (1.22 cubic inches) of nitric acid of 1.2 sp. gr., and filtered into a beaker-glass. The filtrate is diluted to 180 to 200 cubic centimeters (10.98 to 12.2 cubic inches), and stirred. The platinum spiral *a* (Fig. 50), weighing about 16 grammes (246.92 grains), is now placed in the beaker-glass. A cone of platinum foil (Fig. 49), weighing about 20 grammes (308.65 grains), is suspended over this from a stand in such a manner that, when rich ores are to be tested, the cone hangs, at the utmost, 1 centimeter (0.39 inch) above the foot ring *b* of the spiral, but only 0.5 centimeter in case of poorer ores, and that a part of the cone shall project above the liquid. The cone is connected by means of a wire conductor with the negative electrode, and the spiral with the positive. The beaker-glass should be covered with a glass plate, cut into halves, and each half perforated with a hole for the wires to pass through. The strength of the galvanic current used is generally such that 90 to 100 cubic centimeters (5.49 to 6.1 cubic inches) of water-gas will be developed in 30 minutes in the voltameter from diluted sulphuric acid (1 : 12), and as much as 180 cubic centimeters (10.98 cubic inches) for rich cupriferous substances. After an electrolytic action of 12 to 18 hours the liquid is examined in order to ascertain whether the whole of the copper has been precipitated, by adding some water, and stirring. In case it still contains copper, the bright portion of the platinum cone, now partly

Fig. 49.

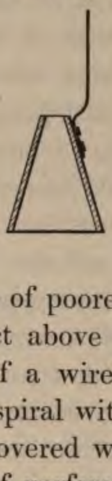
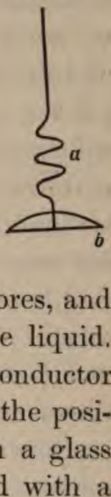


Fig. 50.

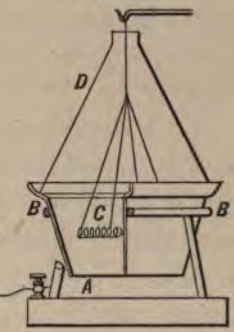


submerged, will be covered with a red film of copper. If no more copper is separated, the beaker-glass is placed in a spacious porcelain dish, and the acid liquid it contains is displaced by adding water until all acid reaction disappears (or the liquid is removed with a siphon, and water is added from a wash-bottle until gas ceases to develop at the positive electrode). The cone of platinum is then taken out and placed in a beaker-glass with water. It is then rinsed off with hot water, next placed in a beaker-glass filled with absolute alcohol, or washed with it, and finally laid upon blotting paper, and dried in an air-bath at about 94° C. (201.2° Fahr.). (If the operator has some experience this can be done quicker upon a piece of sheet-iron heated over a lamp, or by holding the cone in the hot air arising from a large platinum or silver dish heated by the flame.) After it has cooled off the cone is weighed; and, as its weight had been accurately ascertained before the operation, the weight of the copper will be given by the increase in weight of the cone, from which the copper can then be dissolved by hot nitric acid. Dark spots upon the red copper indicate the presence of *arsenic*, *antimony*, or *selenium*. If only small quantities of the first two are present, they are very slowly precipitated, or not at all, from a strong acid solution, if the current is interrupted, while the fluid possesses still a faint bluish color. The presence of much iron prevents a complete precipitation of the copper, as it (Cu) is dissolved by the ferric sulphate while ferrous oxide is formed, the action of free nitric acid upon which, produces blackish-brown circles around the platinum cone. When this is observed it is a sure indication that the process of precipitating the copper has not taken place properly. In this case the assay sample is dissolved in 40 cubic centimeters (2.44

cubic inches) of nitric acid, and 360 cubic centimeters (21.96 cubic inches) of water, using a stronger galvanic current, giving 120 cubic centimeters (7.32 cubic inches) of water-gases in *Volta's* apparatus; or, what is still better, the copper is precipitated from an acid solution by sulphuretted hydrogen, and the copper sulphide dissolved in 30 cubic centimeters (1.83 cubic inches) of nitric acid of 1.2 specific gravity. It is then digested until the sulphur shows yellow. 200 cubic centimeters (12.2 cubic inches) of water are added, and the fluid is then electrolyzed.

Herpin[1] dissolves 1 gramme (15.43 grains) or more of the assay sample in nitric acid, evaporates nearly to dryness, dissolves in a small quantity of dilute sulphuric acid, and dilutes the solution to 60 to 70 cubic centimeters (3.66 to 4.27 cubic inches). The solution is poured into the platinum dish *A* (Fig. 51), and the conducting stand *B* of the dish is connected with the negative electrode, the platinum spiral *C* with the positive electrode, and the liquid electrolyzed after the funnel *D* has been placed in position. When the copper has been precipitated, the fluid is poured from the dish. This is rinsed out first with water, and next with alcohol, then dried and weighed, the copper being determined from the increase of weight.—*Hampe's*[2] method of testing *refined copper:* 25 grammes of copper are dissolved in a beaker, at a moderate temperature, in 200 cubic centimeters (12.2 cubic inches) of water, and 175 to 180 cubic centimeters (10.68 to 10.98 cubic inches) of nitric acid of 1.2 specific gravity. To this are added 25 grammes of previously diluted sulphuric acid (about 4 cubic centimeters (0.24 cubic inch) more than is required for transforming the nitrate into sulphate). The liquid is then evaporated to dryness in a porcelain dish on the water-bath. The dry mass is heated upon a

Fig. 51.



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[1] B. u. h. Ztg. 1875, p. 394. Dingler, ccxvii. 440.

[2] Preuss. Ztschr. xxi. Lief. 5. Fresenius' Ztschr. xiii. 176.

sand-bath until the volatilization of the free sulphuric acid is complete. The dish is then covered, and, after the mass has become cool, 20 cubic centimeters (1.22 cubic inches) of nitric acid are added to it. Water is now allowed to flow gradually into the dish until the entire volume amounts to 350 cubic centimeters (21.35 cubic inches). The silver is removed by the addition of an equivalent quantity of hydrochloric acid. The liquid is electrolyzed in a vessel capable of holding from 400 to 450 cubic centimeters (24.41 to 27.6 cubic inches). The strength of the galvanic current used should be such that 130 cubic centimeters (7.93 cubic inches) of oxyhydrogen gas—it may vary from 90 to 180 cubic centimeters (5.49 to 10.98 cubic inches)—are developed in 30 minutes in the voltameter from diluted sulphuric acid (1 : 12). The liquid is electrolyzed for about 72 hours, the subsequent manipulations being the same as above described.—The presence of small quantities of *bismuth* in the precipitated copper can be determined by the following process: The copper is dissolved in nitric acid, concentrated hydrochloric acid in large excess is added, and the nitric acid boiled away. The excess of hydrochloric acid is evaporated on the water-bath, a large quantity of boiling water is added, and, after 24 hours, the precipitate, consisting of basic bismuth and copper salts, is filtered off. The filtrate is dissolved in hydrochloric acid, and again precipitated with water. This precipitate is dissolved in nitric acid, and the copper contained therein separated by ammonium carbonate.

3. *Determination of the copper in the form of cuprous sulphide.*[1]—This demands the absence of metals precipitable from acid solutions with sulphuretted hydrogen, and the metallic sulphides of which are not volatilized in a heated current of hydrogen (*silver*, *lead*, *bismuth*, *cadmium*, *antimony*, *tin*). During the dissolving process, *lead* may be separated by sulphuric acid, *antimony* and *tin* by nitric acid; *mercury* and *arsenic sulphide* are volatile. In case a considerable percentage of *nickel* is present, nickel sulphide will be precipitated with sulphuretted hydrogen, which can only be prevented by using a large excess of acid.

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[1] Bestimmung des Kupfers in kupferhaltigen Kiesen, Abbränden und ausgelaugten Abbränden in Fresenius' Ztschr. xvi. 335.

1 to 5 grammes (15.43 to 77.16 grains) of the assay sample are decomposed with nitric acid or *aqua regia*. The residue of sulphur is removed by hydrochloric acid and potassium chlorate. The liquid is then diluted with water and the silver precipitated with common salt. The solution is then filtered, heated to about 80° to 100° C. (176° to 212° F.), and saturated with sulphuretted hydrogen, the precipitate filtered, after standing about one hour, and quickly washed with hot water. The filter is dried between blotting paper and next quickly in a hot sand bath. The precipitate is detached from it and the filter with the addition of some sulphur incinerated upon the cover of a tared porcelain evaporating dish which contains the copper sulphide. This, after an addition of sulphur (0.5 gramme, 7.71 grains), is strongly heated for about half an hour, while a current of hydrogen or illuminating gas is conducted to it through an opening in the cover, or through a perforated mica plate, which has been placed upon the crucible. Cu_2S with 79.85 per cent. of copper will be formed. (If a current of carbonic acid is used, too much Cu_2S is obtained, in consequence of the less complete decomposition of the cupric sulphide.)

Of *nickel coins*, 0.5 grammes (7.71 grains) are dissolved in nitric acid and evaporated to dryness with 1 cubic centimeter (0.06 cubic inch) of sulphuric acid, the residue is dissolved in 200 cubic centimeters (12.2 cubic inches) of boiling water, and the solution precipitated with sulphuretted hydrogen, etc.

Apparatus[1] *for igniting in a current of hydrogen* (Fig. 52).—*a*, a vessel with water and zinc; *b*, funnel for pouring in sulphuric acid; *c*, discharge pipe for the gas; *d*, drying tube of calcium chloride; *e*, gas discharge-pipe; *g*, porcelain crucible with perforated cover (*Rose's* crucible); *l*, lamp. Fig. 53—*a*, gas generating flask with funnel tube *b*; *c*, wash vessel with concentrated sulphuric acid; *d*, calcium chloride tube; *e*, bulb-tube for the reception of the substance. It is advisable to pass the gas first through a solution of potassium permanganate, and next, a solution of sodium hydrate to free the hydrogen from hydrocarbons, etc.

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[1] Sicherheitsvorrichtung für Wasserstoffentwicklungsapparate in Fresenius' Zeitschr. xvi. 93. Poggendorf's Ann. 1876, Heft. 10.

Fig. 52.

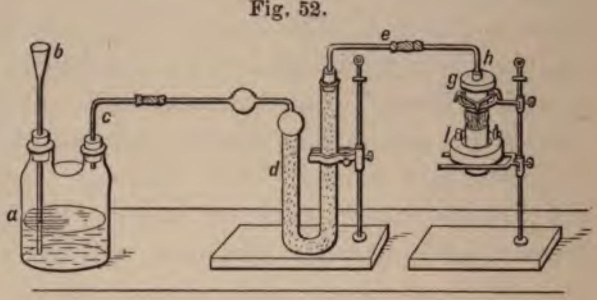
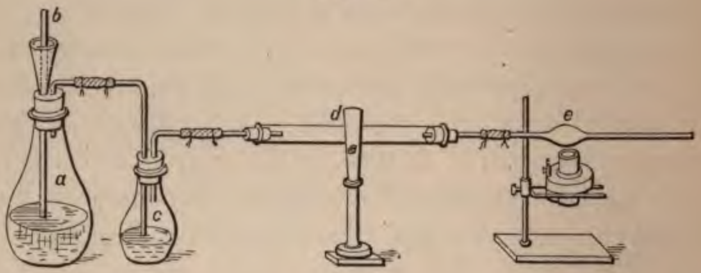


Fig. 53.



4. *Assay with sulphocyanide.*[1]—This method allows of the presence of nickel, zinc, iron, and arsenic; 0.5 to 1 gramme (7.71 to 15.43 grains), or more, of the assay sample is dissolved in nitric acid and evaporated to dryness with sulphuric acid until the free sulphuric acid is *completely* expelled.

The dry mass is now dissolved with a little water and a large quantity of sulphurous acid added to the cold solution. Potassium sulphocyanide is then gradually added until white copper sub-sulphocyanide is precipitated (if too much potassium sulphocyanide is added at one time, the black sulphocyanide is formed which is only gradually reduced to sub-sulphocyanide by sulphurous acid.) A sufficient quantity of the sulphocyanide salt has been added when the fluid commences to assume a reddish-brown color. This coloration is caused by the presence of iron, but the fluid will, in a short time, become entirely colorless. The precipitate is allowed to settle and is then decanted with cold water until a solution of silver nitrate is not rendered turbid by the wash water. It is then filtered upon a previously weighed filter and dried for 12 hours at 105° to 110° C. (221° to 230° F.), and weighed ($100\ Cu_2S_2Cy_2 = 52.2\ Cu$). In order to control the correctness of the result, the filter is incinerated by itself, the copper sulphocyanide is heated in a porcelain crucible to decompose the sulphocyanide, and is then ignited with sulphur in a current of hydrogen, and treated as on page 121.

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[1] Fresenius' Ztschr. xvii. 55.

Nickel coins.—1 gramme (15.43 grains) is dissolved in 10 cubic centimeters (0.61 cubic inch) of nitric acid of 1.18 specific gravity, and evaporated to dryness with 1 cubic centimeter (0.061 cubic inch) of concentrated sulphuric acid. The dry mass is dissolved in a little water, and to the solution is added 50 cubic centimeters (3.05 cubic inches) sulphurous acid solution, and 2 grammes (30.87 grains) of potassium sulphocyanide. After having stood for 12 hours it is filtered, etc. For the determination of *nickel* in the filtrate see "NICKEL."

Copper alloyed with tin (bronze).—1 gramme (15.43 grains) of the alloy is dissolved in a mixture of 6 cubic centimeters (0.36 cubic inch) of concentrated nitric acid of 1.5 specific gravity with the addition of 3 cubic centimeters (0.18 cubic inches) of water. When the action of the acid has ceased the contents of the dish is heated for a time, and next treated with 40 cubic centimeters (2.44 cubic inches) of boiling water. It is then allowed to settle. The sediment, consisting of stannic oxide, containing 78.7 per cent. of tin (free from copper) is washed and weighed. If other proportions of acid are used the stannic oxide will be cupriferous. If black specks, which will indicate nickel sulphide, show themselves upon solution, some hydrochloric should be added to the nitric acid. *Arsenic*, when copper is precipitated with potassium sulphocyanide, remains in the filtrate. Some sulphurous acid is added, then boiled away, and the arsenic precipitated with sulphuretted hydrogen. *Iron* remains with the nickel, and may be separated by twice dissolving and precipitating with ammonia. *Sulphur* is determined by barium chloride.

B. Volumetric assays.[1]—A large number of precipitating methods have been recommended: according to *Pelouze*, with sodium sulphide; according to *Galetti*, by means of potassium ferrocyanide; according to *Schwarz*, with potassium xanthate; and, according to *Vollhard*, with potassium sulphocyanide. Of reducing methods, the following are recommended, viz.: according to *de Haen*, with sodium hyposulphite and potassium iodide; according to *Weil*, with protochloride of tin; according to *Parkes*, with potassium cyanide; according to *Schwarz*, with ferric chloride and potassium permanganate, and others. The method with *potassium cyanide* is largely used in smelting works, for the reason that it is easily executed, and affords a sharp final reaction. *Weil's* method with protochloride of tin is also simple, and both methods are particularly well adapted for a further test of the impure, black, precipitated copper obtained in the Swedish assay (pp. 113, 114).

1. *Parkes' assay with potassium cyanide.*[2]—Thi

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[1] Mohr, Lehrb. der Titrirmethode, 1874, pp. 214, 262, 319, 473, 665; B u. h. Ztg. 1871, p. 222 (Pelouze); 1869, p. 19; 1877, p. 207 (Schwarz) 1870, p. 447; 1872, p. 26; Oestr. Zeitschr. 1871, No. xvii.; Oestr. Jahrb der Bergakademien u. s. w. Bd. xx. p. 133 (Weil); Fresenius' Ztsch xvii. 53 (Rhodanprobe).

[2] B. u. h. Ztg. 1867, p. 102; 1869, p. 18; 1871, p. 222; 1872, p. 207, 347, 419. Oestr. Jahrb. xx. 133.

method is based upon the reduction of an ammoniacal solution of copper by treatment with potassium cyanide. The blue color of the solution disappears and colorless cyanide of copper and ammonium is formed ($4CuN_2O_6 + 8KCy + 2Am_2O = 4CuCy + 2AmCy + 8KNO_3 + 2Am,CyO$). Foreign metals which give a solution of peculiar color with ammonia (*nickel*, *cobalt*) or which form a colorless solution (*zinc*, *manganese*) exert a disturbing effect, as do also such as produce a precipitate which it is difficult to free from hydrated oxide of copper in washing (*ferric oxide*, *alumina*). *Lead*, *silver*, *tin*, and *antimony* may be removed in advance. The presence of *arsenic* is harmless, provided no ferric oxide is present at the same time, since ferric arsenate is soluble in ammonia. This method is much used in practice, and gives sufficiently accurate results, provided the same conditions are always observed (*i. e.*, uniform dilution, the use of the same quantities of acids and ammonia, etc.).

The following quantities of ore are dissolved:—

10 grammes	(154.32 grains)	of ore,	when	it	contains	0.1 to 1	per cent.	Cu.
5 "	(77.16 ")	"	"	"	"	1 to 5	"	"
2.5 "	(38.58 ")	"	"	"	"	5 to 30	"	"
1 to 0.5"	(15.43 to 7.71)	"	"	"	"	30 to 80	"	"

The assay sample is dissolved in nitric acid and, if it contains lead, is evaporated nearly to dryness with sulphuric acid. It is then diluted with water to the bulk of $\frac{1}{4}$ liter (0.44 pint) and (if the above mentioned injurious foreign metals are present) precipitated from the acid solution with sulphuretted hydrogen. The precipitate of copper sulphide is filtered, and washed on the filter with a solution of sulphuretted hydrogen. It is then rinsed off from the filter into the same flask, which was used for the solution, and is heated with 10 cubic centimeters (0.61 cubic inch) of concentrated nitric acid of 1.41 specific gravity until the sulphur is seen to separate in the form of globules. Ammonia is now added until precipitation takes place, then 20 cubic centimeters (1.22 cubic inches) of ammonium carbonate solution (1 : 10) are added. The quite clear solution is filtered off from the sulphur into a beaker glass. The sulphur remaining in the flask is treated with hydrochloric acid and potassium chlorate until it is entirely dissolved. It is then evaporated to dryness on the sand bath, and the residue is treated as above with water, ammonia, and carbonate of ammonium, and filtered into the principal solution. The filter, from which the precipitate of copper sulphide was washed off, is spread out in a beaker glass. Water is poured over it, a few drops of nitric acid are added to it, and it is then boiled for a few minutes. Ammonia and carbonate of ammonia are added as above, and the solution is likewise filtered into the original solution, which is then diluted to the bulk of ½ liter (0.88 pint) and should have only a faint odor of ammonia. 20 cubic centimeters (1.22 cubic inches) of the liquid are taken and titrated with a solution of potassium cyanide until the color has so nearly disappeared that only a faint violet tint remains (best seen in a porcelain dish) and which entirely disappears in from 1 to 2 minutes (by titrating at 60° C. (140° F.) the percentage of copper found will be somewhat less, but more accurate).

The potassium cyanide is standardized as follows, and should be used in as fresh a condition as possible, viz.: 5 grammes (77.16 grains) of potassium cyanide are dissolved in ¼ liter (0.44 pint) of water, and 1 gramme (15.43 grains) of electrolytic copper, in nitric acid. The solution is supersaturated with ammonia and ammonium carbonate, and diluted as above, to the bulk of 1 liter (1.76 pints). 100 cubic centimeters (6.1 cubic inches) of the solution will then contain 0.1 gramme (1.54 grains) of copper from which the potassium cyanide may be standardized.

Copper precipitated with iron (p. 112), or with zinc (p. 114). Mansfeld copper schist (Kupferschiefer) may be examined by this method by dissolving 5 grammes (77.16 grains) of the precipitated copper (p. 115) in from 8 to 16 cubic centimeters (0.48 to 0.97 cubic inch) of nitric acid of 1.2 specific gravity. The solution is gently heated, allowed to cool, and is then supersaturated with 10 cubic centimeters (0.61 cubic inch) of a mixture of 1 volume ammonia and 2 volumes of water. It is titrated with potassium cyanide, 1 cubic centimeter (0.061 cubic inch) of which represents 0.005 gramme (0.077 grain) of copper.—It is advisable to preserve the solution of potassium cyanide in the dark, in a tightly stoppered flask of green glass.

2. *Fleitmann's method with ferric chloride.*[1]—Copper precipitated by zinc, as described on p. 114, is dissolved in a mixture of ferric chloride and hydrochloric acid. The solution should be made in a glass flask furnished with a rubber valve (Fig. 10, p. 39), and with the addition of a little sodium carbonate to expel the air. Protochloride of iron ($Cu + Fe_2Cl_6 = CuCl_2 + 2FeCl_2$) is formed, which is titrated with potassium permanganate until a pinkish coloration remains permanently.

The standard of the solution of potassium permanganate is fixed as follows: 0.2 to 0.3 gramme (3.08 to 4.63 grains) of piano wire, containing at an average 0.4 per cent. carbon, is placed in a flask provided with a mark at 200 cubic centimeters (12.2 cubic inches) and dissolved in diluted sulphuric acid, the air being excluded. It is allowed to cool off, and is then diluted to 200 cubic centimeters (12.2 cubic inches) with distilled water previously boiled. Solution of potassium permanganate (prepared as below) is then added, drop by drop, to 100 cubic centimeters (6.1 cubic inches) of the solution of iron until the light rose-red coloration remains permanently. This operation is repeated with the remaining 100 cubic centimeters of iron solution. From these titrations the value of the permanganate may be calculated. The flask, during the operation, should be placed upon white paper, as this will aid in accurately recognizing the tint of the solution which indicates the end of the reaction. The solution of potassium permanganate is made by dissolving 4.5 grammes (69.44 grains) of potassium permanganate in 1 liter (1.76 pints) of water, when 1 cubic centimeter (0.061 cubic inch) of the solution will correspond to 0.008 gramme (0.12 grain) of iron. It is advisable to have 1 cubic centimeter of the permanganate solution (0.061 cubic inch) correspond to from 6 to 10 milligrammes (0.92 to 0.15 grain) of iron, as with this strength, one drop of the solution will produce a perceptible tint. 1 equivalent Cu (31.50) = 2 equ. Fe (55.90). Instead of using dissolved iron, the strength of the permanganate solution may be determined with the double sulphate of iron and ammonia, containing 6 eq. H_2O, and representing 14.286 per cent. of metallic iron.

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[1] Ann. d. Chem. u. Pharm. xcviii. 141.

If the original solution of copper contains nitric acid, bismuth, or lead, it is precipitated with ammonia in excess and filtered. The copper is then precipitated with the aid of heat, by means of finely divided zinc, in ammoniacal solution.

C. Colorimetric methods.[1]

1. *Heine's assay for poor ores and products* (*slags, etc.*). *Standard solutions*, containing, respectively, 0.025, 0.02, 0.015, 0.01, and 0.005 gramme to every 120 cubic centimeters (7.32 cubic inches) of liquid are prepared either by dissolving a known weight of copper and diluting this as much as may be necessary to obtain the separate gradations of copper, mentioned above, in equal volumes of

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[1] Dingler, 1857, p. 436. Berggeist, 1867, No. 27.

the liquid; or by directly weighing off the above mentioned quantities of electrolytic copper and dissolving each with a few drops of nitric acid in a graduated vessel, adding ammonia in excess and diluting the clear, blue fluid with distilled water to 120 cubic centimeters (7.32 cubic inches). The solutions are then introduced into oblong sample-glasses, having exactly the same form and sectional area, about 50 millimeters (1.96 inches) long, 50 millimeters (1.96 inches) wide, and 110 millimeters (4.33 inches) high. They should be closed with ground-glass stoppers, and marked on the outside with figures, representing the strength of the solutions; in this case, 0.025, 0.02, 0.015, 0.01, and 0.005 gramme Cu in 120 cubic centimeters (7.32 cubic inches). The solution to be tested is prepared in the following manner: 5 grammes, (77.16 grains), or more, of ore are dissolved, from which an ammoniacal copper solution is prepared in the same manner as in the assay with potassium cyanide (p. 125). The volume of the solution is measured to cubic centimeters, and it is then poured into an empty standard-glass. The intensity of the color of the solution is compared with that of the standard solutions, the glasses being held against a sheet of white paper, and it is observed with which of them it corresponds in intensity of color. The percentage of copper is then calculated, due consideration being given to its volume.

Suppose 5 grammes (77.16 grains) of ore had been used, and 300 cubic centimeters (18.3 cubic inches) of solution had been obtained, the color of which corresponded to the standard liquid containing 0.02 gramme in 120 cubic centimeters (7.32 cubic inches); the copper in 5 grammes would then amount to 1 per cent. ($120 : 0.02 = 300 : x$).

If the assay solution is darker than the darkest standard solution, it is diluted to a known volume with water, until it corresponds with one of the standards. Should the reverse be the case, the solution under examination is evaporated to a known volume. This method is less acurate where high percentages are involved, as errors in observation will be multiplied. It is best to determine in this way from 1 to 2 per cent. of copper at the utmost.

In precipitating copper solutions containing iron, by means of ammonia, the *ferric hydrate*[1] always retains some copper. This error is equalized by adding, in preparing the standard solutions, a quantity of iron corresponding about to the percentage of iron in the assay sample (assay of slag in Swansea). Organic substances, in presence of nitric acid, produce with ammonia a greenish tint, which exerts a disturbing effect in comparing the color of the copper solution (therefore, copper-schist should be ignited and filters incinerated before they are brought in contact with nitric acid). Ammoniacal solutions which may become turbid (for instance, if diluted with ordinary water containing lead) are allowed to become clear, and are filtered once more.

2. *Jaquelin-Hubert's method for considerable percentages of copper.*—Only *one* normal or standard solution of known strength is used. This is compared with the solution under examination in a graduated glass tube (calibrated). If richer than the standard, the assay solution is diluted to correspond with the former; and if poorer, the standard solution is correspondingly diluted, until an equal intensity of color has been obtained. From the relative volumes the percentage of copper is then readily calculated. The standard solution contains 0.5 gramme (7.71 grains) of copper in 1000 cubic centimeters (61.02 cubic inches). As errors of observation may easily occur, a gravimetric or volumetric assay is frequently preferred for larger percentages of copper.

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[1] B. u. h. Ztg. 1869, p. 302.

III. SILVER.

30. PRINCIPAL ORES.

Native silver; amalgam, Ag and Hg, with 26.5 to 86 Ag; *antimonial silver*, Ag and Sb, with 59 to 84 Ag; *silver telluride* (*hessite*), Ag_2Te, with 62.79 Ag; *silver glance*, Ag_2S, with 87.1 Ag; *brittle silver ore* (*stephanite*), Ag_5SbS_4, with 68.56 Ag; *ruby silver* (*pyrargyrite*), $Ag_3(Sb, As)S_3$, with 65.38 to 59.98 Ag; *miargyrite*, $AgSbS_2$, with 35.86 Ag; *polybasite*, $Ag(Cu, Fe, Zn)_9Sb(As)S_6$, with 64 to 75 Ag; *stromeyerite*, CuAgS, with 53 Ag; *horn silver*, AgCl, with 75.26 Ag; *iodyrite* (*silver iodide*) AgI, with 46 Ag; *bromyrite* (*silver bromide*) AgBr, with 57.45 Ag.

31. ASSAYS FOR NON-ALLOYS.[1]

The fire-assay methods are based upon the principle of decomposing the silver ore by means of lead or lead oxide, collecting the silver thus set free with an excess of the lead, the slagging off of foreign substances by suitable fluxes, and the cupellation of the lead button to separate the silver. The collection of silver in a lead button is effected, according to the nature of the foreign admixtures, either in a scorifier (scorification assay) or in a crucible (crucible assay).

The crucible assay permits of a large quantity of assay sample being used (which reduces the error from a loss of silver), and for this reason, it may be especially recommended for poor ores and such compounds as are free from antimony and arsenic (chloride, bromide, and iodide of silver and slags), and also for ores or sweepings of a very complex composition. The *scorification assay* is better adapted for ores containing sulphur, antimony, and arsenic, though likewise for other ores, so that this may be called an assay of general applicability; but, nevertheless, for the first-named ores, etc., the crucible assay is simpler and cheaper and the result is more quickly attained. In *America* the *crucible assay* is chiefly used, while the *scorification assay* is preferred in *Germany*, although neither possesses any material advantage over the other.[1]

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[1] Blossom, Gold and Silver Assays, in Am. Chemist, Jan. 1871, p. 250; Aaron, Pract. Treatise on Testing and Working Silver Ores, San Francisco, 1877.

Wet assays are less commonly used.

I. *Fire Assays.*

A. Collecting the silver with lead.

1. *Scorification assay.*—This consists of an oxidizing fusion of the ores with lead, which becomes oxidized and yields up oxygen to the metallic sulphides, arsenides, and antimonides, forms a slag with the oxides thus formed and with the earths which may be present. The slagging off of basic earths is promoted by an addition of borax glass. The following points must be taken into consideration in preparing the charge.

a. The quantity of lead to be used will depend on whether the metallic sulphides, arsenides, and antimonides are easily or difficultly decomposed by lead oxide (p. 79), or whether they are entirely absent. Either granulated lead free from silver, which is measured (p. 31), is used, or argentiferous lead, whose percentage of silver is deducted from the assay by placing the silver button obtained from a corresponding quantity in the balance pan with the weights in weighing.

Lead sulphide is the easiest to decompose, next the *sulphides of iron and zinc*, and then *copper sulphide*. The most difficult are the *sulphurized and arsenized nickel and cobalt ores.*

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[1] B. u. h. Ztg. 1867, p. 102; 1874, p. 68; 1877, p. 232.

b. The quantity of borax depends on the degree of infusibility of the gangue (silicic acid and aluminous substances require but little, and lime and magnesia, much borax) and of the metallic oxides which are formed (ferric oxide, zinc oxide, stannic oxide, and nickel and cobalt ores require much, oxides of copper, bismuth, etc. but little).

In all cases, but *little* borax should be taken at first, to prevent the entire surface of the charge from being covered, as this would exclude the air. If *more borax* is necessary, it is added before the final heating. Much antimony and zinc oxide cause the cupels to become full of cracks.

c. The number of samples to be taken to control the accuracy of results will vary according to the richness of the ores, their want of uniformity, etc., from 2 to 10 or more.

d. If the ore contains less than 1 per cent. of silver, 5 grammes (77.16 grains) or about $\frac{1}{6}$ A. T.[1] are taken for a charge, if more than 1 per cent., 2.5 grammes (38.58 grains) (from $\frac{1}{10}$ to $\frac{1}{12}$ A. T.), and of very rich ores, 1 to 0.5 gramme (15.43 to 7.71 grains) or about $\frac{1}{30}$ to $\frac{1}{60}$ A. T. In assaying very poor ores, the lead buttons obtained by scorification are concentrated by further scorification.

The following table gives some examples of various *charges*:—

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[1] Assay ton = 29.166 grammes.

Argentiferous substances.	Test lead: times the quantity of substance.	Borax glass: per cent.	Remarks.
Amalgamation residues	12 to 15	to 15	Two assay samples, each 5 grammes (77.16 grains, or say $\frac{1}{6}$ A. T.) are scorified, and the two buttons obtained are cupelled.
Antimonial ores . . .	16	200	Assay sample 1 25 grammes, about $\frac{1}{25}$ A. T.
Antimonial silver . .	32	300	The same.
German-silver, or China silver	20 to 24	to 40	2.5 grammes (38.58 grains, $\frac{1}{10}$ to $\frac{1}{12}$ A. T.).
Arsenical ores . . .	to 16	to 50	Require a high temperature in scorifying.
Galena, pure	6	0 to 15	
" siliceous. . .	to 11	20 to 30	
" zinciferous . .			
Lead speiss	10 to 20	15 to 25	2.5 grammes (38.58 grains, $\frac{1}{10}$ to $\frac{1}{12}$ A. T.) are used for the charge. The buttons obtained from two assays are again fused, with a little borax at first, then with addition of more.
Lead matt	9 to 20	12 to 25	
" nickeliferous . .	11 to 14		
Bronze	20 to 24	20 to 25	2.5 grammes (38.58 grains, from $\frac{1}{10}$ to $\frac{1}{12}$ A. T.) are used and repeatedly scorified.
Darrkupfer	18 to 20	10	Charge same as above.
Milling silver ores—			
common	12 to 15	to 15	
basic	8	25 to 50	
acid	8	0 to 20	
siliceous	12 to 14	10 to 15	
Iron, cast iron . . .	8 to 12	2 to 3 1 glass	The iron is first oxidized in the muffle by admitting air, or by means of nitric acid.
Fluthafter	12 to 15	15	Several assays, as many as 30, are made, and the lead buttons obtained are scorified into one, and this is cupelled.
Refined copper . . .	18 to 20	1 to 5	Charge 2.5 grammes (38.58 grains, $\frac{1}{10}$ to $\frac{1}{12}$ A. T.).
Sweepings, argentiferous and auriferous	8 to 9	0 to 20	See p. 22.
Hearth bottoms . . .	8	10 to 20	
Gun-metal	20 to 24	20 to 25	Charge 2.5 grammes (38.58 grains, $\frac{1}{10}$ to $\frac{1}{12}$ A. T.).
Kiehnstöcke	18 to 20	10	The same.
Cobaltiferous ores . .	20	15 to 20	
Cupriferous ores . . .	10 to 20	10 to 15	

Argentiferous substances.	Test lead: times the quantity of substance.	Borax glass: per cent.	Remarks.
Copper matt	12 to 15	10 to 15	
Brass	20 to 24	15 to 20	The same.
Nickeliferous ores . .	20	15 to 20	The same.
Furnace deposits. . .	12 to 14	10 to 15	
Raw matt	10 to 12	to 30	Only a small quantity of borax at first.
Slags.	12 to 15	10 to 15	The same as fluthafter.
Black copper	18 to 20	10 to 15	Charge 2.5 grammes (38.58 grains, $\frac{1}{10}$ to $\frac{1}{12}$ A. T.).
Residue from the amalgamation of black copper and extraction of silver	8 to 10	1 to 10	The same.
Zinciferous ores . .	10 to 16	15 to 25	Fusion at a high temperature.
Argentiferous zinc . .	16	16	Charge 1.25 grammes (19 29 grains, about $\frac{1}{25}$ A. T.) of zinc oxide with 16 parts of lead and 16 parts of borax.
Stanniferous ores . .	20 to 30	15 to 25	They are scorified several times.
Argentiferous tin . .	16	16	Charge 1.25 grammes (19.29 grains, about $\frac{1}{25}$ A.T.) of stannic oxide, with 16 parts of lead and 4 parts borax glass.

The quantity of test lead required according to the foregoing table is measured or weighed off, and divided approximately into two parts. The accurately weighed assay sample is mixed with one-half of the lead in the bottom of the scorifier, and the mixture is covered over with the remaining part of the lead, and finally the borax is added. The charged scorifier is placed in a strongly heated muffle, the mouth of which is closed, and a strong draft kept up for the purpose. The lead will soon commence to fuse, and in sinking down absorb silver from the ore. This, on rising to the surface, is roasted off, and is strongly oxidized by the lead oxide formed at the same time. During the oxidation slag is formed from the edges of the scorifier, by the combination of another part of the lead oxide with the metallic oxides and earths that are present, and with the borax. The time required for this first heating (roasting and fusing) is from 25 to 30 minutes when a completely fused ring of slag, without adherence to the edge of the scorifier, will show itself. (Refractory ores, such, for instance, as contain zinc, cobalt, and nickel, or which contain considerable lime, require the strongest heat, and, should they not completely fuse even then, a sufficiently large addition of borax must be made before the final heating.) The second period is that of the "*scorification*." The fire is checked, and the mouth of the muffle is opened, until, by the continued oxidation of the lead and foreign metallic compounds, the entire surface of the lead is covered with slag. This will require from 20 to 30 minutes. The mouth of the muffle is then closed, the heat raised, and a final heating of 10 to 15 minutes is given to render the slag completely fluid. The scorifier is now taken from the furnace, and allowed to cool in the scorifier or poured off. After cooling off, the lead button is carefully freed from slag and *hammered* into the form of a cube, with truncated edges and corners. The time required for the entire operation will be from $\frac{3}{4}$ to $1\frac{1}{4}$ hour, according to the degree of fusibility of the ores. When the ores are very poor, a number of the lead buttons which have been obtained are placed on a scorifier, either with or without borax, and scorified as indicated above. If necessary the *concentration* is repeated until finally *one button* containing the entire percentage of silver is obtained. A second scorification is also advisable, in case the *button be too large*, or when it contains much *antimony*, *arsenic*, or *copper*. A percentage of *nickel* will exert a disturbing influence in cupellation. A cupel will usually absorb about its own weight of litharge, from which the proper size of the button may be estimated.

Hungary:[1] Two samples each of 2.5 grammes (38.58 grains, about $\frac{1}{12}$ A. T.) are each charged with 8 to 16 parts of granulated lead, in such a manner that one-third of it is mixed with the ore and some silver flux (2 parts of melted *Villach* litharge and 1 part of calcined borax), and covered with the remaining two-thirds. *Lower Harz:* 5 grammes (77.16 grains, ab. $\frac{1}{6}$ A. T.) are mixed in the scorifier with 50 grammes (771.61 grains) of granulated lead and 0.75 to 1 gramme (11.57 to 15.43 grains) of borax, and covered with 0.5 gramme (7.71 grains) of borax. The cupels consist of 3 parts wood-ash and 1 part bone-ash.

With chloridized ores: A charge of 5 to 10 grammes (77.16 to 154.32 grains, $\frac{1}{6}$ to $\frac{1}{3}$ A. T.) of the ore is scorified with ten times its weight of lead, and cupelled to determine the percentage of silver. In a second sample the silver chloride is dissolved out by lixiviation with sodium hyposulphite, and the residue is scorified, etc., for the estimation of the unchloridized silver.

2. *Crucible assay.*—In this method of assaying, the ore is fused with lead oxide (litharge, white lead), in order to decompose the metallic sulphides (p. 78), with fluxing agents (potash, borax), for slagging off oxide and earths, and with some carbonaceous substance (charcoal powder, flour, argol, black flux), for reducing the lead which then collects the silver. The quantity of the reducing agent will depend on the reducing power of the ore. It should be so gauged that the lead button produced shall not be too large in order to prevent a notable loss of silver in cupellation. Ores containing a large percentage of antimony, arsenic, and zinc should be previously roasted, to prevent the formation of oxysulphides, etc., which are difficult to decompose, and which carry silver along with them into the slag; 5 grammes (77.16 grains, ab. $\frac{1}{6}$ A. T.) of the finely powdered ore are mixed in a crucible with 40 grammes (617.29 grains) of a flux consisting of 1.5 parts of lith-

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[1] B. u. h. Ztg. 1871, p. 254.

arge, 0.15 part of potassium carbonate, and 0.08 part of flour. This is covered with 25 grammes (385.80 grains) of litharge, and this in turn with about 4 grammes (61.73 grains) of borax. The crucible should have smooth sides, a diameter of 45 millimeters (1.77 inches) at the top, and of 30 millimeters (1.18 inches) at the bottom, an inside height of 145 millimeters (5.70 inches), and outside of 165 millimeters (6.49 inches). The charged crucible is then placed in the furnace upon a bed of glowing coke, which should cover the grate to a height of from 100 to 150 millimeters (3.93 to 5.9 inches), and is then surrounded up to its rim with wood charcoal. The furnace is left open for the first quarter of an hour. After the coal has been replenished, the cover of the furnace is put on and the fusing is continued for a quarter of an hour longer. The crucible is then taken out, allowed to cool, and the lead button, which should weigh from 20 to 25 grammes (308.64 to 385.80 grains) is freed from slag. (Chile.) The same quantity of litharge as used for the assay is fused at the same time, but without ore, with fluxing agents. The lead button is freed from slag and cupelled, to determine the percentage of silver, which must be deducted from the assay-button. *Or*, 5 grammes (77.16 grains, ab. $\frac{1}{6}$ A. T.) of ore are fused with 50 grammes (771.61 grains) of lithage, 2 grammes (30.87 grains) of argol, 12 grammes (185.19 grains) of sodium carbonate, with a covering of common salt, and the resulting lead button is cupelled. White lead is sufficiently free from silver.

Mexican charge:[1] 20 grammes (308.64 grains, about $\frac{2}{3}$ A. T.) of ore, 66 grammes (1018.53 grains) of litharge, the same quantity of sodium carbonate, and 3 grammes (46.30 grains) of charcoal powder are mixed in a crucible of the above dimensions and covered with 20 grammes (308.64 grains) of common salt. 40 assays are put in the furnace and fused, first, for a quarter of an hour, during which the furnace is left open. It is then closed, and the assays are fused for a half an hour longer. 66 grammes (1018.53 grains) of litharge are reduced, and the amount of silver found is deducted.—*Another charge* is as follows: 16 grammes (246.92 grains, about $\frac{1}{2}$ A. T.) of ore, 48 grammes (740.75 grains) of litharge, 60 grammes (925.94 grains) of sodium carbonate, 16 to 20 grammes (246.92 to 308.65 grains) of powdered charcoal, which is omitted when a large percentage of iron pyrites is present.—*Another charge* is: 2 grammes (30.87 grains, about $\frac{1}{15}$ A. T.) of ore, 25 grammes (385.80 grains) of litharge, 10 grammes (154.32 grains) of sodium carbonate, and a covering of common salt.—*Spain:*[1] 5 grammes (77.16 grains, about $\frac{1}{6}$ A. T.) of ore are fused in a crucible with 20 grammes (308.65 grains) of litharge, borax, black flux, or potassium carbonate and flour, with a covering of common salt.—*English charge:* 10 grammes (154.32 grains, about $\frac{1}{3}$ A. T.) of ore, the same quantity of sodium carbonate, 50 grammes (771.61 grains) of litharge, and 1 to 1.5 grammes (15.43 to 23.15 grains) of argol, with a covering of 10 grammes (154.32 grains) of common salt and the same quantity of borax.—*Gold and silver sweepings:* 10 grammes (154.32 grains) of borax and the same quantity of argol are poured into a crucible with smooth sides, 75 millimeters (2.95 inches) in diameter on the top, and 110 millimeter (4.33 inches) high; upon this are placed 20 grammes (308.64 grains) of litharge. The sides of the crucible are moistened by gently breathing upon them, it is then inclined and turned in such manner that litharge adheres to the sides about $\frac{2}{3}$ the way up. 15 grammes (231.48 grains) of potassium carbonate and 25 grammes (385.80 grains) of sweepings are then added, and the entire mass is thoroughly mixed together with a broad spatula. It is then covered with 10 grammes (154.32 grains) of sodium carbonate, and upon this comes a layer of common salt 12 millimeters (0.47 inch) thick, and finally 5 grammes (77.16 grains) of litharge are strewed around the sides of the crucible. The furnace is filled with pieces of gas-coke the size of a walnut, the coke, when it is in a glow, is stamped down, and from 6 to 8 crucibles are placed in the fire in such a manner that the edge of the crucible projects but little above the coke. The furnace is then closed, and the heat gradually increased until the charge ceases to swell up. The temperature is then quickly raised for from 15 to 20 minutes, until the charges have become thin fluid and flow bright and uniform. The operation is therefore finished in about half of an hour. The crucibles are now allowed to cool, and the buttons weighing about 22 grammes (339.51 grains) are freed from slag and then cupelled. (In assays of large lots of ore five assays are made.)—*Other charges for sweepings:* 25 grammes (385.80 grains, about ⅘ A. T.) of sweepings, the same quantity of minium, 35 grammes (540.13 grains) of flux (prepared by mixing 600 parts of potassium carbonate, 200 parts borax, 100 parts glass-galls, 100 parts soda, 30 parts saltpetre, 30 parts powdered charcoal); or, 25 grammes (385.80 grains) of sweepings, 20 grammes (308.64 grains) of common salt, the same quantity of sodium carbonate and of potassium carbonate, 25 grammes (385.80 grains) of litharge, 10 grammes (154.32 grains) of argol, and the same quantity of powdered glass; or; 25 grammes (385.80 grains) of sweepings, 20 grammes (308.64 grains) of litharge, 25 grammes (385.80 grains) of flux (1 part potassium carbonate and 1 sodium carbonate), and a covering of common salt. The charge is kept in the furnace until quiet fusion, requiring about three-quarters of an hour (Braubach).—*Slags:* 10 grammes (154.32 grains, about ⅓ A. T.) of slag, 150 to 160 grammes (2314.85 to 2469.17 grains) of litharge, 2.5 grammes (38.58 grains) of quartz, and 0.25 gramme (3.85 grains) of charcoal powder. The charge is fused in a crucible for 20 minutes after the development of gas in the furnace has ceased, and the buttons of two charges are cupelled together (Pribram).—*Freiberg:* 7.5 grammes (115.74 grains, about ¼ A. T.) of slag are mixed in a crucible with 11 to 15 grammes (169.76 to 231.48 grains) of potassium carbonate and flour, 19 to 30 grammes (293.21 to 462.97 grains) of granulated lead are strewed on top, and the charge is fused for 3 hours in the furnace.—*Refuse from stamping mills:* 10 grammes (154.32 grains, about ⅓ A. T.) of substance are mixed in a high crucible (Fig. 39, p. 66) with 60 to 120 grammes (925.94 to 1851.88 grains) of potassium carbonate and flour; upon this is placed 50 to 100 per cent. of borax, next 10 to 15 grammes (154.32 to 231.48 grains) of granulated lead, and finally a covering of common salt. It is fused in the muffle-furnace for 1½ to 2 hours.

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[1] B. u. h. Ztg. 1874, p. 86.

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[1] B. u. h. Ztg. 1868, p. 26.

3. *Combined lead and silver assay.*—This method of assaying is used for oxidized lead products (litharge, skimmings, dross), and for galena with at least 30 to 40 per cent. of lead, and not over 0.12 per cent. of silver. Such galena, after the assay with potassium carbonate,

as described on page 92, is fused to a lead button, which is then cupelled. This method is not satisfactory after the preliminary assay with iron (p. 86), as the iron sulphide will retain silver in varying quantities in the slag.

Litharge: 20 grammes (308.64 grains, ab. ⅔ A. T.) litharge, 15 grammes (231.48 grains) potassium carbonate and flour, and 5 to 6 per cent. of powdered charcoal, with a covering of common salt, are placed in a crucible and fused in the muffle-furnace. If necessary, several of the buttons are concentrated by scorification (p. 136) and cupelled. *Skimmings* and *dross* are charged in the same manner; but, should they be very impure, the lead buttons must be scorified with 4 to 8 times their weight of granulated lead before they are cupelled.

B. Cupellation of the argentiferous lead (*assaying by the cupel or cupellation*).—The lead buttons obtained according to A Nos. 1 to 3 (pp. 132–141) are subjected to oxidizing fusion. During this operation the lead is first oxidized; the lead oxide yields up oxygen partly to the foreign metals, and partly combines with their oxides; and if they are not too refractory (as, for instance, ferric and stannic oxide, etc.), enters with them into the cupel.

If the lead contains much *antimony* and *zinc*, it is apt to cause cracks in the cupels; *copper* colors them green, and the percentage of copper may be quantitatively determined within certain narrow limits by the intensity of the color.

The cupels (Fig. 44, p. 68), first carefully wiped out with the fingers, then all extraneous matter blown out, are thoroughly heated (ignited) in the muffle. They are arranged in two rows, six in each row, in the front third of the muffle.[1] The lead buttons are now laid hold of with a pair of forceps (Fig. 46*b*, p. 74) and gently deposited, first in the front and then in the back row of crucibles. The mouth of the muffle is closed, the fire is urged on, and the lead fused as quickly as possible. The lead will at first be covered with a dull, dark film. As soon as this disappears, and the lead shows a lustrous, fuming surface, the mouth of the muffle is opened (with the exception of a low piece of charcoal which is left in it) for the admission of air to oxidize the lead, and the temperature is lowered, by ceasing to stir the fire, to lessen the loss of silver. Cold scorifiers are placed in several rows above each other back of the cupels, and, if the argentiferous lead is very rich, the cooling-iron (Fig. 48, p. 74), which should be frequently cooled off in water, is moved to and fro closely over the cupels. The correct temperature is indicated by the arising lead fumes *whirling* over the assays, and not slowly creeping over them or rising straight up; by the cupels glowing dark brown, by small scales of crystallized litharge (plumose litharge, Federglätte) showing themselves on the inner edge, and by a bright but not too wide border of litharge upon the lead. If the temperature is *too low*, the fume creeps slowly over the cupels; these become too dark, a dark rim of litharge is formed, and the lead ceases to "drive." This is called a "*freezing*" of the assay. Frozen assays, if again brought to "driving" by a higher heat, and generally some addition of lead, cause a considerable loss of silver. By *too high* a temperature, the lead fumes arise up straight, the cupels glow too brightly, neither plumose litharge (Federglätt) nor a rim of litharge shows itself, and the loss of silver increases. At the *correct* temperature small beads of litharge float upon the surface of the lead button, the heat to which it is subjected causing convection currents, which give the button a motion from below upwards

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[1] Hempel's gas-furnace with oxidizing apparatus in Fresenius' Ztschr. xvi. 454; xviii. 404.

("driving"), and a convex surface from which the luminous beads and patches of litharge are continually thrown towards the sides, and are there absorbed by the cupel. As soon as these patches upon the diminishing lead become larger towards the end, the scorifiers, which had been placed back of the cupels, are removed, the cooling with the cooling-iron is stopped, and the fire is urged on. Towards the end the last of the lead is absorbed, and the silver button presents itself colored with all the tints of the rainbow (*brightening, coruscation*), which gradually disappear, whereupon the button solidifies. (If the temperature has been too low, the surface of the button is dull and yellow, and the unabsorbed litharge forms lumps or scales about it; while otherwise, it is pure silver-white on top and bottom, and very lustrous.) If the bead is large the cupels are allowed to cool off slowly by drawing them to the front of the muffle, to prevent the buttons from "*sprouting*" or "*spitting*." They are then taken out upon a piece of sheet-iron, and the buttons (generally of 99.7 to 99.8 per cent. pure silver) are detached by means of a pair of pincers (p. 75), and brushed off with the button-brush (p. 75). Faultless buttons brightened at a sufficiently high temperature (smaller ones are round, larger ones hemispherical) should have a silvery lustre on the surface, be dull silver-white and crystalline on the bottom, and without rootlets. They are then weighed. The globule of silver obtained from the separately scorified and cupelled granulated lead, if this was not entirely free from silver, is placed in the scale-pan containing the weights; or, the silver percentage of the lead having been determined once for all, it may be deducted from the results obtained.

Assays of silver should agree very closely, and if properly conducted are of great accuracy. The results of duplicate assays should not differ from each other more than one-half ounce Troy per ton of two thousand pounds. Should a greater difference be found, an additional assay should be made.

Smaller losses of silver occur in scorifying (which for this reason should be continued as long as possible, so as to obtain small lead-buttons requiring but a short time for "driving") than in cupelling, by the volatilization of silver, and by the silver oxide passing into the cupel with the lead oxide by which it has been oxidized (loss by cupellation, Kapellenzug). The loss increases with the temperature and the size of the button, and for this reason, with the time required for cupelling, as well as with the porosity of the cupels. The percentage of loss is considerably larger (2 to 4 per cent.) in smaller buttons (poorer ores) than in larger buttons (1 to 1¾ per cent.), but in the first case can generally not be determined by the balance. The smallest loss occurs in gas muffle-furnaces (Fig. 29, p. 55), which have no vent-holes in the muffle. In case the ore contains *tellurium*, the button spouts at the moment of solidification, after brightening, and fine globules of the metal are thrown off and lost.

II. *Wet Assays.*

Balling's volumetric assay.[1]—2 to 5 grammes (30.87 to 77.16 grains) of galena are fused in a porcelain crucible with 3 to 4 times its weight of a mixture of equal parts of saltpetre and soda. This is allowed to cool off; the contents of the crucible are lixiviated with water, heated in a porcelain dish, and filtered. The residue is decomposed with diluted nitric acid, and evaporated to dryness. The dry mass is then taken up with water acidulated with nitric acid, heated and filtered. Ferric sulphate, or iron-alum is added to the cooled-off filtrate, and it is then titrated with a $\frac{1}{10}$ normal solution of ammonium sulpho-cyanide, which is prepared by dissolving 0.7 to 0.75 gramme (10.8 to 11.57 grains) of the salt in 1 liter (1.76 pints) of water. The titer is made to correspond with a silver solution of a known strength, in such a manner that 1 cubic centimeter (0.061 cubic inch) of the ammonium sulpho-cyanide solution corresponds exactly to 1 cubic centimeter (0.061 cubic inch) of silver solution. The latter is obtained by dissolving 1 gramme (15.43 grains) of chemically pure silver in nitric acid, and diluting it to a bulk of 1 liter (1.76 pints). The presence of copper in small quantities is not injurious, and of that of lead is rather favorable, as the white precipitate of lead sulphate, which is formed after the ferric sulphate has been added, makes the recognition of the final reaction sharper. A large percentage of iron gives a brownish-colored solution, which does not permit a distinct recognition of the final reaction. Larger quantities of copper must be previously removed, but cobalt and nickel, if the operator has some experience, admit of an easy recognition of the final reaction by a yellowish-brown color. The assay requires about three hours, and may be especially recommended when no muffle-furnace is at hand, or if only one sample is to be assayed for which it would not be worth while to heat a furnace. The permissible error allowed in the smelting works at Pribram is 0.03 per cent. from ores carrying 0.30 to 0.60 per cent. of silver, and the differences obtained by this assay vary within narrower limits than those allowed for dry assays. The assays give equally good results for all degrees of richness, if the galena is pure and contains but little iron.

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[1] Fresenius' Ztschr. xiii. 171; Oestr. Ztschr. 1879, No. 27.

32. ASSAYS OF ALLOYS.

These are generally executed by the *wet method* only for silver containing copper (as, for instance, coins). The *dry method* is mostly used for other alloys, and they are either assayed by direct cupellation without scorification, with an addition of lead in case the sample does not already contain a sufficient quantity.

A. Dry assays.

1. *Lead bullion.*[1]—10 to 20 grammes (154.32 to 308.64 grains), according to the percentage of silver in it, are directly worked off on the cupel; but if the lead is impure (slag lead, zinciferous lead), it must be previously scorified. Poor lead is slagged off on the scorifier in quantities of from 40 to 50 grammes (617.29 to 771.62 grains), and the resulting buttons are concentrated into one button by scorifying them once or several times, and the collected button thus obtained is cupelled. (For instance, 10 assays of 50 grammes each of *Pattison's* granulated lead, which is very poor in silver, are concentrated to one button.) The cupels used for a charge of from 10 to 20 grammes (154.32 to 304.64 grains) of granulated lead, have an outer diameter of 49 millimeters (1.92 inches) on the top and 39 millimeters (1.53 inches) on the bottom, a clear width of 37 millimeters (1.45 inches), a total height of 23 millimeters (0.9 inch), and a depression of 17 millimeters (0.66 inch).

2. *Silver amalgam.*—5 grammes (77.16 grains) of the assay sample are weighed off in a watch-glass and gradually heated in the cupel for 1½ hours in a moderately heated muffle. After all the mercury is volatilized, 6 or

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[1] Abtreiben mit Sauerstoff in B. u. h. Ztg. 1868, p. 351.

7 times the quantity of lead is added and the charge cupelled (p. 141).

3. *Copper poor in silver* (black copper, refined copper).—2.5 grammes (38.58 grains) are scorified with 18 to 20 times the quantity of lead and cupelled, whereby the cupel will be colored dark green. Pure or plumbiferous copper may also be immediately cupelled with 16 to 18 times the quantity of lead in one charge.

4. *Cupriferous silver or fine silver*[1] (coins, refined silver, etc.).—The sample is directly cupelled (*mint assay*) with a quantity of lead free from silver (simple weights of lead in the form of small sticks or round or half-round pieces are used, but not granulated lead), corresponding to the percentage of copper. Smaller and finer cupels (*mint cupels*) are used. They consist, like the French cupels, either of powdered bone-ash alone, or of bone-ash and lixiviated wood-ash, which makes them more porous. They are placed in a small muffle-furnace (*mint* or *fine assay-furnace*, Fig. 28, p. 54), for the better regulation of the heat; or, what is still better, in a gas-furnace (Fig. 29, p. 55). Where the percentage of silver is not known, the approximate percentage[2] is first determined by a preliminary assay (cupelling with 16 times the quantity of lead), or by the touchstone,[3] so that the proper quantity which experience has proven to cause the

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[1] Probe über der Lampe in Fresenius' Ztschr. 1879, p. 82.

[2] Coins: The German Reichsmark, German Thaler, Austrian and South German Gulden, 900 thousandth parts Ag; English silver coins, 925; French small silver coins, 835; 5, 2, 1, ½, ¼ franc pieces, 900; German nickel coins, 75 Cu and 25 Ni; German copper coins, 96 Cu, 3 Sn, 1 Zn; French small coins (5 cent.), 95.21 Cu, 3.18 Sn, 0.44 Zn, 0.25 Ni, 0.58 Pb, 0.06 Ag. Swiss coin (5 cent.), Cu 58.920, Zn 23.700, Ni 11.561, Ag 5.146, Pb 0.326, Co 0.286.

[3] Dingler, cxxiii. 366; Ann. de Chemie et Phys. 1875; Bay, Ind. u. Gew. Bl. 1869, p. 130; Kick, techn. Bl. 1873, p. 35; Fresenius' Ztschr. 1878, p. 142.

smallest loss of silver may be used. With silver coins, in which the silver percentage is known, the preliminary assay is unnecessary.

The numbers given in the following table may be taken as a guide:—

DEGREE OF FINENESS OF THE ALLOY. Silver in thousandth parts.	MULTIPLES OF LEAD.
1000 to 950	4
950 " 900	6
900 " 850	8
800 " 750	12
750 " 650	14
600 " 0	16 to 17

A sample of the alloy to be assayed, weighing 0.5 gramme (7.71 grains), is hammered out and cut up into fine shreds. Generally two assays are made at one time. The samples from bars are taken from the upper and lower side, and are obtained from pieces weighing about 2.5 grammes (38.58 grains), which have been cut out from the lower and upper sides of the bar on opposite ends. The samples are wrapped up in cornets of fine letter-paper, and placed upon a small assay-plate. When lead granules are not at hand, a piece of stick lead is weighed out and placed in two thoroughly glowed-out cupels, standing in the centre of the strongly heated muffle-furnace (Fig. 28, p. 54). The Paris *mint cupels* have been especially recommended for the purpose. Their outer diameter is 26 millimeters (1.02 inches) on the top, and 22 millimeters (0.86 inch) on the bottom; clear width, 21 millimeters (0.82 inch); total height, 14 millimeters (0.55 inch), with a depression of 8 millimeters (0.31 inch). The mouth of the muffle is closed with a coal, and as soon as the lead "drives" the cornet containing the sample is placed in the cupel, the mouth of the muffle again closed, and the assay allowed to "drive." The mouth of the muffle is now again opened, with the exception of a low piece of coal or small piece of iron, the cupels are drawn forward towards the mouth of the muffle, and the temperature is lowered by partly closing the draught of the furnace, or also by cooling with a small cooling-iron (Fig. 48, p. 74), until a small ring of litharge and some plumose litharge (Federglätte) appear. The assays are now gradually pushed back, and the temperature is raised by opening the draught of the furnace, so that the assay may "brighten" sufficiently hot, during which the ring of litharge will disappear, but the plumose litharge (Federglätte) remain. The crucibles are now drawn, forward towards the mouth of the muffle, and allowed gradually to cool off to prevent "spitting." When sufficiently cool they are taken from the muffle, and the buttons are removed by means of a pair of pincers and brushed. In successful assays the surface of the button is smooth, with a silvery lustre on the top, and a dull silver-white color on the bottom. If the operation has been conducted at too low a temperature, the surface is dull, and has a bluish tint, and the bottom is covered with a yellowish or greenish coating of lead oxide. If the temperàture has been too high, the button is dull in some places, very lustrous in others, the surface is sunken, it is liable to spit, exhibits rootlets, adheres stronger to the cupel, and is porous toward the bottom. The buttons are then weighed, and, in assays of top and bottom samples, either the average percentage or the lowest percentage is given. The loss from absorption by the cupel (Kapellenzug) is added.

Bars with over 980 thousandths of silver show no difference, if the work has been carefully done. To 725 thousandths they show a difference of ½ to 3 thousandths; from 720 to 710 thousandths, again, no difference, or only an infinitely small one (certain chemical combinations seem to be formed at this percentage); but the greatest differences occur at 400 to 200 thousandths fineness. Very considerable differences may occur if the bars or buttons have been badly fused. The silver button contains about ·2 thousandths of lead.

Correction Table for the Absorption by the Cupel, determined by the French Commission on Coinage and Medals.

True quantity of silver.	Loss to be added, thousandths.	True quantity of silver.	Loss to be added, thousandths.
1000	1.03	500	4.68
975	1.76	475	4.50
950	2.50	450	4.31
925	3.25	425	4.13
900	4.00	400	3.95
875	4.07	375	3.61
850	4.15	350	3.27
825	4.22	325	2.94
800	4.30	300	2.60
775	4.41	275	2.58
750	4.52	250	2.56
725	4.64	225	2.55
700	4.75	200	2.53
675	4.73	175	2.12
650	4.71	150	1.70
625	4.70	125	1.29
600	4.68	100	0.88
575	4.68	75	0.66
550	4.68	50	0.44
525	4.68	25	0.22

In *Freiberg* somewhat different results have been obtained. With refined silver the loss by absorption by the cupel was found to be 0.0015 to 0.002, and in alloys of medium richness the loss was greater than that stated in the table; for instance, with 750 thousandths and 16 weights of lead, the loss was 5.55 thousandths, but with 11 weights of lead it accorded with the table, 4.52 thousandths. According to *Plattner*, fine silver with 5 times the quantity of lead frequently gives a loss up to 0.009, refined silver with 937 thousandths and 5 times the quantity of lead, 0.0042 to 0.0059; refined silver with 687 to 750 thousandths and 14 times the quantity of lead, 0.0073 to 0.0083.

B. Wet assays.

They are used for *refined silver* and *coin alloys* of copper and silver. Compared with the fire assay, they allow of an accurate determination of the degree of richness to within 0.5, and even to 0.1 thousandths. They are more frequently *volumetric* than *gravimetric* assays.

1. *Volumetric assays.*

a. Gay-Lussac's method with sodium chloride.[1]—This method is based upon the precipitation of silver from a nitric acid solution by means of a standard solution of sodium chloride. For this purpose a *normal solution of common salt* is required, 100 cubic centimeters (6.1 cubic inches) of which will precipitate 1 gramme (15.43 grains) of chemically pure silver. There is further required a *decinormal solution of common salt*, 10 times weaker than the first, and a *decinormal solution of silver*, consisting of a solution of silver in nitric acid, containing 1 milligramme (0.0154 grain) of silver in 1 cubic centimeter (0.061 cubic inch) of solution.

Preparation of the assay solution.—The degree of richness of the silver is approximately determined by a preliminary assay, the fine assay (p. 147) being generally chosen for the purpose. 4 to 6 thousandths parts the amount of silver found by this assay, are added to the result. It is generally preferred to assume the degree of richness a few thousandths higher than is actually the case, and to base the calculation for the quantity of assay sample required upon this, as, to effect the more rapid settling of the silver chloride, it is preferable to add, during the titration, a few thousandths from the decinormal solution of salt than to be obliged to add from the decinormal solution of silver. The quantity of alloy containing 1 gramme (15.43 grains) of silver which is to be taken is then calculated (for instance, if the preliminary assay gives a percentage of 897 thousandths, then 1.115 grammes of alloy containing 1.000 gramme of silver should be taken, $1000:897=x:1000$). The sample in the form of shavings or granules is placed in a numbered flask, together with 6 to 7 cubic centimeters (0.36 to 0.42 cubic inch) of nitric acid free from chloride, and dissolved, either on a water or sand bath. The flasks in which the samples are dissolved are from 10 to 15 centimeters (3.93 to 5.9 inches) high, and 5 to 5½ centimeters (1.96 to 2.16 inches) wide. If several assays are to be made, it is advisable to dip the flasks, which are arranged upon a stand (Fig. 54), into hot water. (A black residue may be gold or sulphide of silver; should the latter be the case, some concentrated nitric acid is added and the fluid heated, or sulphuric acid used.) The nitrous acid formed is then driven out of the flask by means of a small bellows with curved extremity, and the contents of the flask is treated with the normal solution. But as the influence of the temperature upon the volume of the normal solution of common salt must be taken into consideration, its titer must always be determined on the same day the assays are to be made, with 1 gramme (15.43 grains) of pure silver + 1 to 2 cubic centimeters (0.061 to 0.12 cubic inch) decinormal solution of silver, in order to be able, for the above mentioned reason, to use decinormal solution of salt for the final titration. The silver solution is then titrated by placing the glass flask in the metal cylinder *C* (Fig. 55) standing upon the sliding carriage *B* (*Sire's* apparatus[1]). The glass cock *c* (a pinch-cock may be used instead) is then opened, and,

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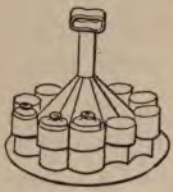
[1] Gay-Lussac, Vollst. Unterricht über das Verfahren, Silber auf nassem Wege zu probiren, Braunschweig, 1833; Mulder, Silberprobirmethode, Leipzig, 1859; Muspratt's Chem., Bd. vi. p. 477; Bolley, Handb. der techn.-chem. Untersuchung, 5 Aufl. pp. 52, 332; Dingler, cxci. 172.

Fig. 54.



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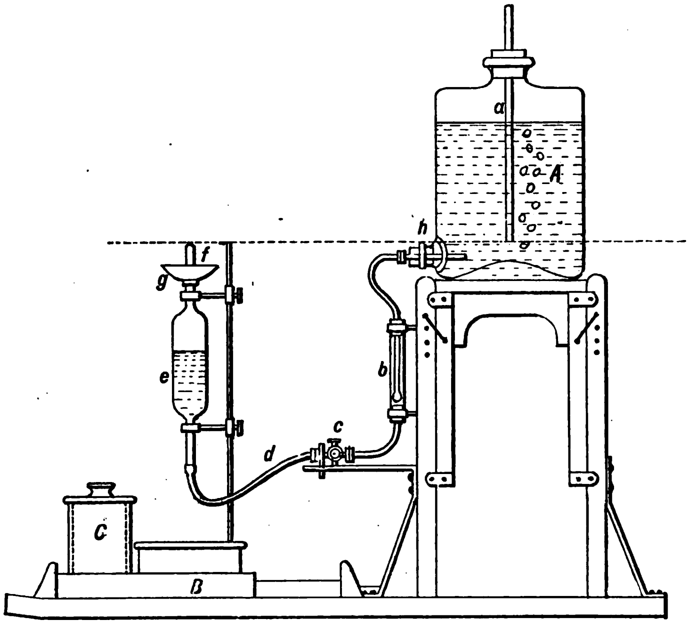
[1] B. u. h. Ztg. 1873, p. 189.

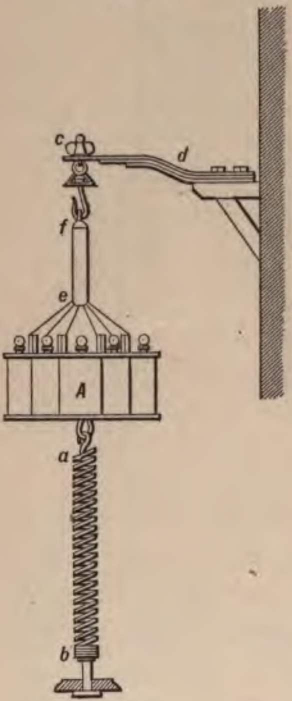
accompanied by the admission of air through *a*, the normal solution of sodium chloride flows from the vessel *A*

Fig. 55.



through *h*, the thermometer tube *b*, and the rubber tube *d*, into the burette *e*. It ascends in this, and a small quantity reaches the saucer *g* through the orifice *f*. The cock *c* is now closed (*h* and *e* may be also directly connected by a rubber tube provided with a clip), and the pipette *e*, which is now filled, will contain exactly 100 cubic centimeters (6.1 cubic inches) of liquid. The index finger of the left hand is now placed upon the mouth *f* of the pipette, the rubber tube *d* is detached from the lower end of the pipette *e*, and the sliding carriage *B*, upon which stands the metal cylinder *C* containing the flask with the solution of silver, is pushed underneath the discharge orifice of the pipette. The index finger is now removed from *f*, and the 100 cubic centimeters (6.1 cubic inches) of the solution of common salt are allowed to run into the flask, care being taken that the pipette does not rest on the neck of the flask. The sliding carriage is then pushed back, the flask is closed with its ground glass stopper, and its contents is cleared by shaking, which is best done by inclosing it in a metal cylinder of proper size for the purpose. If many assays are to be made, it is advisable to use *Gay-Lussac's* or *Mulder's* agitator.

Fig. 56.



Gay-Lussac's apparatus (Fig. 56). —*A*, a stand with cylindrical compartments for the reception of the flasks which are provided with well ground stoppers. The stand is suspended by the handle *e f* to the steel spring *c d*, and is connected below with a spiral spring *a b*. The apparatus is shaken by means of the handle *e f*.

Fig. 57.

1 cubic centimeter (0.061 cubic inch) of decinormal solution is now added to the entirely clear fluid, standing over the precipitate of silver chloride, by means of a graduated pipette contained in a flask (Fig. 57), whereby the point of the pipette should be placed against the neck of the flask containing the silver solution. If turbidity is produced, the silver solution is agitated until it is again

clear, and 1 cubic centimeter (0.061 cubic inch) of the decinormal solution of common salt again added, etc., until the last cubic centimeter which is added does not produce any turbidity. This last cubic centimeter is not taken into calculation, and only one-half of the one previously added. (For the reason stated on p. 151, it is more suitable to use decinormal solution of common salt than decinormal solution of silver for the final reaction).

Calculation.—Suppose the richness of the alloy was found according to the preliminary assay to be 897 thousandths, 1115 thousandths of the sample containing 1.000 gramme (15.43 grains) would have to be weighed off. 1000 cubic centimeters of the decinormal solution of salt = 1 gramme (15.43 grains) of silver. Now suppose 1002.5 cubic centimeters (61.17 cubic inches) of decinormal solution of common salt had been used, 1000 parts of the alloy would therefore contain 899.1 parts of silver.

In case *mercury*[1] should be present, sodium acetate (0.5 gramme (7.71 grains) to 5 thousandths of mercury) is added, which will prevent the mercury from being precipitated by the sodium chloride solution; or the mercury is previously volatilized by heating the sample in a small graphite crucible in the muffle. For *bismuth* some tartaric acid is added. In case *tin* is present, the sample is dissolved in sulphuric acid instead of nitric acid. According to *Thorpe*, only 2 parts of silver chloride freshly precipitated, and 0.8 part that has been blackened by exposure to light, are dissolved in 100,000 parts of nitric acid.

Preparation of the normal solutions.—A completely saturated solution of common salt is prepared, of which, if the salt used is entirely pure, 170 cubic centimeters (10.37 cubic inches) contain 54.15 grammes (835.66

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[1] B. u. h. Ztg. 1870, p. 303.

grains) of common salt. These 170 cubic centimeters (10.37 cubic inches) are diluted to the volume of 10 liters (17.6 pints). 100 cubic centimeters (6.1 cubic inches) of this solution correspond to 0.5415 gramme (8.3566 grains) of common salt, which will completely precipitate 1 gramme (15.43 grains) of pure silver. The true standard is obtained by pouring 100 cubic centimeters (6.1 cubic inches) of the solution of common salt into a solution of 1 gramme (15.43 grains) of chemically pure silver. This is agitated by shaking until it becomes clear, and the number of thousandths of common salt or silver which remain free are exactly determined by the addition of an observed volume of very dilute salt solution of known strength, or of a decinormal solution of silver, and from this the quantity of water or of common salt is calculated which must be added to obtain the correct standard. When this addition has been made, a new test is made with the standard solution and the decinormal solution prepared from it, and this is continued until the solution does not show a perceptible variation from the correct standard. The decinormal solution of common salt is prepared by pouring 100 cubic centimeters (6.1 cubic inches) of the standard solution of salt into a flask capable of holding 1 liter (1.76 pints) and filling it with water to the liter mark. For the decinormal solution of silver, 1 gramme (15.43 grains) of fine silver is dissolved in 5 to 6 grammes (77.16 to 92.59 grains) of nitric acid, which is then diluted with water to 1 liter (1.76 pints).

b. Volhard's assay with sulpho-cyanide.[1]—The solution of silver, which should be free from nitrous acid, mercury, and palladium, and to which has been added some ferric sulphate, is precipitated in the cold with titrated potassium sulpho-cyanide until a permanent red coloration from iron remains, indicating that all the silver has been precipitated. The assay, which is as accurate as *Gay-Lussac's*, is simpler, and can be executed more quickly, and allows at the same time of a determination of a percentage of gold in the same assay sample.

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[1] Volhard, die Silbertitrirung mit Schwefelcyanammonium, etc., Leipzig, Winter, 1878; Dingler, ccxiv 399; B. u. h. Ztg. 1875, p. 83; 1876, p. 405 (Lindeman); Fresenius' Ztschr. xiii. 171; 1878, p. 482.

The standard solution of potassium sulpho-cyanide is prepared by dissolving 10 grammes (154.32 grains) of chemically pure silver in nitric acid free from chlorine, and diluting it to 1 liter (1.76 pints); 50 cubic centimeters (3.05 cubic inches) of this solution are placed in a beaker-glass and diluted with 3 to 4 times its volume of water; 5 cubic centimeters (0.3 cubic inch) of a pure solution of ferric sulphate (1 part of the salt in 10 parts of water) are added to it, and the solution of potassium sulpho-cyanide is allowed to flow to it, under constant stirring, from a burette holding 50 cubic centimeters (3.05 cubic inches) and divided into $\frac{1}{10}$ and filled exactly to the 0 point, until the color of the solution remains permanently red. The assay fluid is prepared by placing 10 grammes (154.32 grains) of the silver in a long-necked flask, capable of holding from 200 to 250 cubic centimeters (12.2 to 15.26 cubic inches). It is then dissolved on the sand-bath in 50 cubic centimeters (3.05 cubic inches) of nitric acid free from chlorine, of 1.2 specific gravity, and diluted with distilled water. Any gold which may be present is then allowed to settle, and the clear silver solution is poured into a flask capable of holding 1 liter (1.76 pints). The residuum is several times digested with a small quantity of nitric acid, and is then decanted with distilled water until the liter flask is nearly full to the liter mark, and the wash-water shows no traces of silver. The flask in which the solution was made is now filled to the rim with water and inverted in a porcelain crucible, to remove the gold contained in it, and the gold, which is weighed to within 0.0002 gramme (0.003 grain), is further treated according to the assay method, which will be given further on. The solution of silver in the liter flask is now diluted to 1 liter (1.76 pints), 50 cubic centimeters (3.05 cubic inches) of it are measured out in a beaker-glass, and titrated with the solution of potassium sulpho-cyanide, after addition of solution of ferric sulphate.

Cobalt and nickel produce peculiar tints which can be easily distinguished from those of the reaction of the silver. In case the sample contains more than 80 per cent. of *copper*, the red coloring is not very perceptible, and *Volhard* and *Fresenius*[1] have given a modification for this emergency; or pure silver may be added to the sample. *Mercury* is removed by previous volatilization, and nitrous acid must be completely removed by boiling, as it decomposes sulpho-cyanic acid, even n the cold, while nitric acid will only do so when heated. A small percentage of chlorine in the solution of potassium sulpho-cyanide does not cause any trouble, but a large amount of it is injurious.

2. *Gravimetric analysis.*—As the solution of common salt evaporates too much in a hot climate, the following method is used in the *East Indies.*[2] 1.22 grammes (18.825 grains) of the alloy are dissolved in nitric acid. The silver is precipitated by hydrochloric acid, and the silver chloride is carefully washed out. The flask is filled with water and inverted in a smooth washing crucible, and then removed. The greatest part of the water is decanted off, and the assay dried, first on the water-bath, and next in an air-bath at 150 to 170° C. (302 to 338° F.), and the silver chloride weighed while still warm.

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[1] Fresenius' Ztschr. xiii. 175.

[2] Dingler, cciii. 97, 203.

C. Hydrostatic assay.—According to *Karmarsch*,[1] the quantity of silver in coins can be determined from the specific gravity L, in thousand parts n, according to the formula—

$$n = \frac{L - 8.833}{0.0016474}$$

This method is not adapted for very fine alloys, nor for such as have been cast and little worked after the casting, as the results obtained are too high.

IV. GOLD.

33. GOLD ORES.

Native gold, with 0.1 to 40 per cent. of Ag, occurring in quartzose veins (gold quartz), and in pyrites (iron or copper pyrites, arsenical pyrites), and disseminated in alluvial deposits (auriferous gravel); *sylvanite* (Au, Ag), Te_2, with 24 to 30 Au and 3 to 15 Ag; *nagyagite*, $PbTe^2$ with PbS and $AuTe_2$, with 6 to 9 Au and 50 to 60.5 Pb; *white tellurium* $(Au,Ag,Pb)(Te,Sb)_3$, with 24.8 to 29.6 Au, 2.7 to 14.6 Ag, and 2.5 to 19.5 Pb.

34. NON-ALLOYS.

Sometimes *mechanical wash assays* are made use of for an approximate determination of the metallic gold contained in poor earthy and gravelly ores. *Dry or fire assays* (*scorification or crucible assays*) are mostly used for a more accurate determination of the percentage of gold in very poor ores; and sometimes the wet assay (*Plattner's assay*) also. The taking of assay samples requires the utmost care on account of the very unequal distribution of the gold in the ores (pp. 20 *et seq.*).

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[1] Dingler, ccxxiv. 565.

A. Mechanical assay by washing, for determining the *approximate* percentage of gold in *earthy and gravelly minerals, poor in gold.* The sample is rubbed as fine as possible and sifted. About 20 grammes (308.64 grains) of it are washed with water in a vanning trough (Fig. 4, p. 29), until the pure gold begins to show itself at the upper end. The quantity is either estimated or weighed, or measured by bringing it into a narrow strip about 0.36 millimeter (0.014 inch) wide (Hungary and Transylvania). Sometimes it is also amalgamated with mercury and ignited in a small crucible (Transylvania, United States).

Montana: 5 kilogrammes (11 pounds) of *earthy* gold ore are taken from the heap, powdered, mixed, and sifted. The coarse gold remaining in the sieve is weighed and assayed by itself; 500 grammes (17.64 ozs.) of the fine sifted matter are placed in the vanning trough (wash-trough) (Fig. 4, p. 29), mixed with some water and 5 grammes (77.16 grains) of mercury, and slowly washed for two hours (if the water shows an acid reaction, some caustic soda is added), and finally some potassium cyanide is added, the amalgam completely purified, mercury is removed by glowing the mass gently in a crucible or retort. The residue is cupelled with lead, and the alloy separated by inquartation and parting; 6 to 8 assays are made and the average is taken.—*Australia:* 1 kilogramme (2.2 pounds) of gravelly gold ore is dead-roasted. It is then placed in an iron mortar and mixed with water to a stiff paste. A tablespoonful of mercury is added and thoroughly rubbed together with the paste; and, after a short time, another tablespoonful. The mass is then washed in an enamelled dish, and the amalgam collected and distilled off. This method will give from 80 to 90 per cent. of the quantity of gold which would be obtained by a fire assay.

B. Fire or fusion assays.—The object of these assays is to collect the gold in the lead (*smelting with lead by the scorification or crucible assay*), and to separate the gold by *cupelling* the auriferous lead button. In case

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[1] B. u. h. Ztg. 1863, p. 271; 1868, p. 127; 1875, p. 311.

the gold button should contain any silver, this can be separated by the wet method by means of nitric acid (*inquartation*). Whether the scorification assay or crucible assay is to be chosen depends principally on the foreign admixtures (earth or gravel), and, as a general rule, the same rules hold good here that were given for silver ores (p. 131).

1. *Smelting the gold with lead.*

a. Scorification assay for ores of every kind.—0.5 to 10 grammes (7.72 to 154.32 grains), according to the degree of richness of the assay sample, are weighed, and, if the material is poor, a sufficient number of assays is made so that the button which is obtained does not weigh less than 0.05 to 0.20 gramme (0.77 to 3.08 grains). The same rule in regard to the quantity of granulated lead and borax is observed as in the silver assays, and the assays are executed in the same manner.

b. Crucible assay.—Poor, earthy, and oxidized ores can be assayed by this method without preliminary preparation, but those containing sulphur, antimony, and arsenic must be previously roasted. It is less adapted for ores rich in gold and copper than the scorification assay. It is simpler and more convenient, as it allows of operating with larger quantities, especially when the substances are poor in precious metal, and is more accurate than the scorification assay, as the losses are distributed among larger quantities of assay sample. The assay sample is fused with granulated lead or litharge and reducing and fluxing agents. Smelting pots or crucibles (Fig. 42, p. 67) the same as in the corresponding silver assays are used. The assay is fused in the ordinary furnace, or in a gas-furnace (p. 59).

α. Substances with earths and oxides (gold quartz, slag, gold sweepings).—They are fused in an unroasted condition.

Sweepings, as stated on p. 140. *American gold ores:* 50 grammes (771.60 grains) of ore, 70 grammes (1080.26 grains) of dry sodium carbonate, 100 to 120 grammes (1543.23 to 1851.88 grains) of litharge (or a corresponding quantity of white lead), and 6 to 8 parts of powdered charcoal. The ore, litharge, and charcoal are first mixed together, and then with the fluxing agent; and, in case sulphur should be present, a small piece of iron wire is added. The charge is placed in a smooth French clay crucible and fused for half an hour at an intense heat in the furnace. It is then poured out, after which the crucible can be used several times more.

The results from 100 pounds of gold quartz by the scorification and crucible assay may be given as follows:—

If 100 pounds of gold quartz give by scorification assay:	They give by crucible assay:
parts of pounds.	parts of pounds.
12.5	12.25
1.5	1.6
0.14	0.14
0.09	0.088.

Rheinsand: 500 grammes (7716.17 grains) of ore are mixed with 200 grammes (3086.47 grains) of soda, 300 grammes (4629.70 grains) of potassium carbonate, and 50 grammes (771.61 grains) of borax. Upon this are scattered 20 grammes (308.64 grains) of granulated lead free from gold, upon this come a thin layer of soda and a covering of common salt.

β. Ores, etc., with combinations of sulphur, antimony, or arsenic.—Larger quantities, 0.5 to 1 kilogramme (1.1 to 2.2 lbs.), are roasted so that buttons weighing not less than 0.05 to 0.20 gramme (0.77 to 3.08 grains) are obtained. The roasting is done in small clay boxes about 200 millimeters (7.87 inches) long, 70 to 90 millimeters (2.75 to 3.54 inches) wide, and 40 to 50 millimeters (1.57 to 1.96 inches) deep. The ore is placed in these boxes and roasted in the muffle, being carefully stirred meanwhile with a stirring rod. Or the ore may be placed upon a plate of sheet iron with upturned edges, which has been previously covered with a coating of clay, reddle, or chalk, and is then roasted over a brazier, or in a furnace until the fumes cease to be evolved (according to Winkler, Tscheffkin, and Merrick, a loss of gold occurs during this operation, which Crookes denies). If copper pyrites, antimony, and arsenic are present, it is best to add charcoal and ammonium carbonate in roasting. The charging and fusing of the roasted sample are done in the same manner as that indicated in the assay for silver (p. 137).

Pyrites poor in gold: 500 grammes (7716.17 grains) of the roasted ore are mixed with the same quantity of granulated lead free from gold, 125 grammes (1929.04 grains) of black flux and the same quantity of glass. The charge is fused for two hours in a Hessian crucible in the furnace. The resulting button is flattened on an anvil and cut up in pieces. The separate pieces are concentrated on a scorifier, and the button thus obtained is cupelled. 500 grammes (7716.17 grains) of ore are roasted and mixed with 125 to 250 grammes (1929.04 to 3858.09 grains) of potassa or soda glass, 125 grammes (1929.04 grains) of black flux, or 250 grammes (3858.09 grains) of potassium carbonate, and 32 grammes (493.83 grains) of flour, then covered with 500 grammes (7716.17 grains) of granulated lead free from silver, and a layer of common salt. The entire charge is put in a Hessian crucible and fused for 2 hours in the furnace, or it is distributed into several smaller crucibles (Fig. 24, p. 49).

Hungarian smelting works: 1 Vienna pound (= 560 grammes = 8642.11 grains) of auriferous substance is roasted upon a clay plate over glowing coals. The charge consists of 3 pounds (= 1680 grammes = 25926.3 grains) of *Villach* red litharge, 2 pounds (= 1120 grammes = 17284.37 grains) of dry potash, $\frac{1}{4}$ pound (= 140 grammes = 2160.53 grains) of resin, and 1 loth (= 14.5 grammes = 223.73 grains) of hard coal. This is mixed and distributed in crucibles in such a manner that on the bottom comes first a spoonful of the mixture, and, upon this, a spoonful of the roasted sample. These are then mixed together; upon this mixture is placed another spoonful of the mixed fluxes, and then a covering of common salt. 115 to 125 crucibles charged in this manner are heated for from 20 to 30 minutes in the furnace, or a small number in the muffle. The resulting buttons are partly cupelled and those buttons which have not brightened are wrapped up in a cornet of lead foil and cupelled together. The auriferous silver obtained must weigh about 10 mint pounds assay weight, and the gold buttons to be separated from this about 0.1 mint pound. Average difference 0.001 mint pound.

2. *Cupellation of the auriferous lead.*—The process is the same as for silver with the exception of a hotter "driving" towards the end of the assay, so that no plumose litharge (Federglätte) remains. If the assay sample is poor, the separate lead buttons are either entirely cupelled or only partly. In the latter case they are wrapped in lead foil and cupelled together. The resulting gold button is then weighed, and, in case it contains silver, this is parted by means of nitric acid. We will only briefly mention the process here, as it will be more thoroughly explained later on in treating of gold and silver alloys (§ 39).

The button is flattened out on the anvil and placed in a flask with a very narrow neck, and then heated with nitric acid of 1.19 specific gravity. *a. When the laminated button breaks up* and brown flakes of gold are separated, this being an indication that a sufficient quantity of silver is present; the heating is interrupted when no more nitrous acid is developed. The gold is allowed to settle, and the liquid is then carefully decanted. It is now washed twice by decantation with boiling distilled water. The flask is then entirely filled with cold water and inverted in a clay crucible, or a small porcelain saucer, and when the gold has dropped into the crucible, the flask is carefully withdrawn over the side. The water is then poured off, the gold dried, the crucible then strongly heated, and finally the adherent gold is removed and weighed. *b. When the flattened button does not break up.*

the acid is poured off and the sample decanted with cold water. The flask is filled with cold water and inverted in a porcelain dish and withdrawn over the side. After the water has been poured off, the button is dried and wrapped, with three times the quantity of silver, in a cornet of lead foil or with granulated lead in a cornet, and cupelled. The button, containing now a sufficient quantity of silver, is parted with nitric acid. In the Upper Harz the percentage of gold is not taken into calculation when 10 assay centner (= 50 grammes = 771.62 grains) contain less than 0.5 parts of pounds (= .25 milligramme = 0.0038 grain) of gold. The buttons obtained from gold ores are, as a rule, richer in gold than in silver, and require an addition of 2 to 2½ times the quantity of silver, while those from auriferous silver ores, pyrites, and matt contain generally less than ⅓ to ¼ of gold and require no addition of silver.

C. Wet assay (*Plattner's* chlorination process[1]).—This is sometimes used for very poor ores: 50 to 200 grammes (771.62 to 3086.47 grains) of earthy or oxidized ore, or *completely* roasted pyrites, are slightly moistened with water and placed in a tubulated glass cylinder, the bottom of the vessel being first covered with pieces of quartz. Here they are treated with chlorine gas for about 1 hour. The gold chloride formed is lixiviated with hot water, and the solution heated to expel the free chlorine. Solution of ferrous sulphate and some hydrochloric acid is added, which precipitates the gold in a metallic state. It is then filtered and washed, the filtrate is dried and cupelled with 5 to 10 grammes (77.16 to 154.32 grains) of granulated lead. *Wagner* recommends the decomposition of the ores with bromine[2] instead of chlorine.

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[1] Plattner-Richter's Löthrohrprobirkunst, 1865, p. 546.

[2] Dingler, ccxix. 544.

35. ALLOYS OF GOLD.

The principal alloys of gold which will be especially considered here are those *with silver*, with *silver and copper*, and with *copper*.

Gold amalgam is distilled in a glass retort, and the residue is carefully scorified with 8 parts of granulated lead (p. 135). *Auriferous lead* and *bismuth* are directly cupelled, but if they contain too small a quantity of gold, they are first slagged off on the scorifier (p. 66). *Auriferous iron, steel*, etc., are dissolved in nitric acid and evaporated to dryness. The dry mass is scorified with 8 to 10 parts of granulated lead and some borax.

A. Alloys of gold and silver, with or without copper.—The separation of gold from silver (called "*quartation*" on account of the proportion of gold to silver as 1 : 3) is done by means of nitric acid. But the silver is only completely dissolved by boiling the acid three times, and when at least 2½ to 3 parts of silver are present to 1 part of gold. When this proportion exists, the gold will also be obtained in a cohering mass having the same form as that of the alloy used (*a small roll, etc.*). If less silver is present, the gold remains argentiferous and, if more, for instance, 4 to 6 silver to 1 gold, the gold is obtained in brownish flakes or as powder (dust gold), while the silver will be completely dissolved by boiling the assay twice with nitric acid, and there is great liability that mechanical losses will occur. If the silver is to be dissolved by boiling the assay but once with nitric acid, at least 8 parts of silver to 1 part of gold must be present. *A preliminary assay* is therefore required for an approximate determination of the percentage of gold, to enable the assayer to fix the required quantity of silver which must be added, and also for the determination of the percentage of copper, in order to find the quantity of lead required to be added to it in removing it by cupellation.

1. As a *preliminary test for alloys free from copper*, may serve—

a. The color of the alloy.—A deep yellow color requires $2\frac{1}{2}$ to 3 times the quantity; light yellow, twice the quantity; and a white color an equal weight of quartation silver.

For an approximate determination, by color, of the richness of the gold button, sample gold-silver buttons 2 to 3 millimeters (0.079 to 0.12 inch) in diameter have been prepared with $\frac{10}{10}$, $\frac{9}{10}$, $\frac{8}{10}$, $\frac{7}{10}$, $\frac{6}{10}$, and $\frac{5}{10}$ of gold. They are placed in depressions in a box with a cover, and each is surrounded with a black ring and then with a white one. Before the comparison is made, the assay button is breathed on, as otherwise its strong lustre would make the estimation less accurate. *Goldschmidt*[1] has attached similar specimen alloys, in the form of small disks upon porcelain, but it is more difficult to compare the buttons with these than with sample buttons of the same shape. If more than 56 per cent. Ag is present, the gold cannot be recognized. 2 per cent. of Ag imparts already a brass color, 50 per cent. a light yellow, and 56 per cent. a white color to the gold.

b. An examination on the touchstone by means of needles, touchstone and nitric acid requires more experience than the above method, and may also be used for alloys containing copper.

2. *Preliminary assay of cupriferous alloys by cupellation.*

a. With lead alone.—250 milligrammes of the alloy cut up into fine shreds or granulated are weighed off and wrapped up in a cornet. This is placed with 16 to 32 times the quantity of lead (4 to 8 grammes, 61.73 to 123.5 grains according to the percentage of copper) in one piece (spherical or hemispherical) in a strongly glowing cupel in the furnace. The cupellation is conducted in the same manner as with the fine assay (p. 147), except that it must "drive" hotter, so that no plumose litharge (Federglätte) remains. The percentage of copper is found from the difference in the weight of the alloy used, and the resulting auriferous silver button. An experienced assayer can then estimate the richness of the alloy in gold by the color of the button after breathing on it, and can thus calculate the quantity of quartation silver to be added for the principal assay. The quantity of lead required for removing the copper by cupellation will be indicated from the difference in weight.

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[1] Fresenius' Ztschr. xvii. 142. B. u. h. Ztg. 1878, p. 208.

The quantity of lead to be taken depends on the *percentage of copper in the alloy*, which must be removed before the quartation. As copper has a greater affinity for gold than for silver, argentiferous gold containing copper requires a larger quantity of lead in cupelling (the maximum is 32 times the quantity) than argentiferous copper (16 to 20 times the quantity).

The following table (Table I.) shows the quantity of lead required for alloys of gold with silver and copper :—

TABLE I.

If the gold in 1000 parts of the alloy amounts to	Equivalent to gold.	Multiples of lead.
1000	24 carat,	8
980 to 920	23½ to 22	12
920 to 875	22 to 21	16
875 to 750	21 to 18	20
750 to 600	18 to 14	24
600 to 350	14 to 8	28
350 to 0	8 to 0	32

Table II. gives the quantity required if the percentage of gold is very small.

TABLE II.

If the silver in 1000 parts amounts to	Equivalent to silver.	Multiples of lead.
1000 to 950	15 loth 9 grän.	4
950 to 900	14 " 9 "	6
900 to 850	13 " 9 "	8
850 to 750	12 "	12
750 to 650	11 "	14
650 to 0	10 " and less	16

b. With an addition of lead and silver.—This process is made use of to avoid the estimation of the quantity of gold in the auriferous silver button by the color. 250 milligrammes (3.85 grains) of the alloy are wrapped up in a cornet, together with 3 times the quantity of silver (750 milligrammes, 11.55 grains), and 16 to 32 times the quantity (4 to 8 grammes, 61.73 to 123.5 grains) of lead, and cupelled. The loss of copper is found from the difference in weight between the resulting button and the alloy weighed plus the addition of silver. The auriferous silver button is laminated and placed in a flask with a long and narrow neck which has been previously well cooled off. The matrass should be from 150 to 180 millimeters (5.9 to 7.07 inches) high, 30 to 50 millimeters (1.18 to 1.96 inches) wide in the belly, and 6 to 8 millimeters (0.23 to 0.31 inch) in the neck. The button is boiled in this with pure nitric acid of 1.19 specific gravity until no more red vapors are evolved, and is then washed twice by decantation with hot water. The flask is then entirely filled with water, a small crucible of clay placed over its mouth, and both crucible and flask are inverted, which causes the gold in the form of a small flake or powder to fall into the crucible. The flask is now raised and quickly drawn away over the edge of the crucible. The gold is then thoroughly dried by igniting it in the crucible. Its weight, plus that of the added quartation silver, deducted from the weight of the auriferous silver button originally employed, gives the percentage of silver in the original alloy, according to which the addition of silver for the assay must be regulated so that the proportion of 1 Au to 2½ or 3 Ag is maintained. For *coins*, the standard of which is known, such preliminary assays are not required.

German,[1] French, and American gold coins contain 900 Au and 100 Cu. Austrian ducats 986, Prussian Friedrichsdor 902, English sovereigns 916, Hanoverian, Brunswick, and Danish pistoles 896 parts of gold. *Pure* gold is prepared by dissolving ducat gold, or gold cupelled with lead and laminated, in cold *aqua regia* (2 parts of hydrochloric and 1 part of nitric acid), by adding the acid gradually, so that, when the solution is complete, there will be no excess of aqua regia. The solution is allowed to stand for several days, for the silver chloride to settle, and is then filtered. It is now diluted, and, if necessary, again filtered in a few days. The filtrate is much diluted, and freshly prepared solution of ferrous sulphate added to it until no more gold is precipitated, and then allowed to stand in a warm place. The fluid is then removed by means of a siphon, the gold placed in a porcelain dish and digested with diluted hydrochloric acid. The dried powder is washed, placed in a clean clay crucible, and fused with some borax and saltpetre.

I. *Roll assay for argentiferous gold.*—This requires the following manipulations:—

a. Preliminary assay as described on p. 167 for determining the percentage of gold and copper in order to fix the quantity of quartation silver and lead to be added.

b. Weighing the assay sample.—Two samples of the alloy, granulated or laminated and cut into fine shreds, each 250 milligrammes (3.85 grains), are accurately weighed out upon an assay balance which must be sensitive to

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[1] Göldner, Farbe der Zwanzig Mark Stüke in Dingler, ccviii. 75.

0.1 milligramme (0.0015 grain). If bars are to be assayed, a sample of 250 milligrammes each is cut from the upper and lower side from opposite ends. The samples are wrapped in cornets.

c. Charging.—The quantity of silver required is weighed off, cut up into fine shreds, and added to the sample. The quantity must be calculated or found from tables according to the results of the preliminary assay. The lead is next weighed off in one piece according to Table I. p. 168.

d. Cupelling.—The lead is placed in thoroughly ignited fine cupels standing alongside of each other in the centre, or more towards the back of a strongly heated mint furnace (Fig. 28, p. 54). The mouth of the muffle is closed until the lead "drives," when it is opened, and the cornets containing the alloy are placed in the cupel. The mouth of the muffle is again closed, and the assay is allowed to "drive," and the operation further conducted in the same manner as in the fine assay (p. 147) with the exception of a stronger heat towards the end. Of the loss of gold in cupelling we will speak later on.

If fine gold with 990 thousandths "drives" too hot, or too cold, the resulting gold button will be one-thousandth too heavy. This is very likely caused by some lead which remains with the gold, and which cannot be completely removed by nitric acid. For this reason a sample of pure gold is generally cupelled with the same quantity of lead at the same time as the principal assay, and the gain in weight of the fine gold is then deducted from the gold percentage of the principal assay. If the button has been brightened too hot, it is apt to crack in laminating.

e. Flattening (laminating) the button.—The button is removed by means of a pair of pliers, brushed off, and the edges carefully pinched with the pliers. It is then laminated with a hammer on a polished steel anvil, having a diameter of 6 to 8 centimeters (2.36 to 3.15 inches). The head of the hammer has on one end a round or square face, smoothly polished, and about 4 centimeters (1.57 inches) in diameter, and on the other end a rounded-off edge. Or, the button after it has been somewhat flattened on the anvil is passed between rollers, being frequently annealed meanwhile on a cupel, or dish, in the muffle. The small oval leaf, into which it is laminated, is about 25 millimeters (0.98 inch) long, 12 millimeters (0.47 inch) wide, and 0.5 millimeter (0.019 inch) thick. The frequent annealing of the button and hammering of the edges is required to prevent the leaf from cracking on the edges. If necessary, the leaves are numbered by means of a punch and hammer. After having been annealed once more, the leaves are rolled with a pair of pliers and dry fingers, into the form of a spiral, or over a glass-rod, into a small roll.

f. Boiling in nitric acid.—One or more of the numbered rolls are placed in a long-necked glass flask, about 150 to 180 millimeters (5.9 to 7.07 inches) long, with a body width of 40 to 50 millimeters (1.57 to 1.97 inches), and a neck width of 15 to 20 millimeters (0.59 to 0.79 inch). Here they are heated with a quantity of nitric acid (about 10 grammes, 154.32 grains) sufficient to fill the body of the flask half-full. The acid should be of 1.2 specific gravity, as, if it is stronger, its action might be too violent and tear the leaf. It should be free from nitrous acid, sulphuric acid, and chlorine, and, if necessary, is freed from chlorine by adding some solution of silver nitrate. The leaves are heated until the fumes of nitrous acid have disappeared. Bumping during the ebullition is prevented by throwing a small splinter of coal, or, what is still better, a completely carbonized pepper-corn, into the flask.[1]

The flask is lifted from the fire by means of a wooden clamp, and the solution of silver carefully poured into a porcelain dish. Nitric acid of 1.3 specific gravity, previously heated to boiling, is now poured upon the leaves, and they are again boiled for 10 minutes. The pouring off of the solution is repeated, and the leaves are again boiled for 10 minutes, with fresh strong nitric acid, previously boiled. This third boiling is sometimes omitted, if the percentage of gold is below 750 thousandths. After the third boiling, according to *Kandelhard's* experiments, such a small residue of silver remains in the gold, that it is equalized by the loss caused by cupellation, and the result will be correct.

(The heating may be done by placing a single flask upon a support, with three legs, and provided with a handle, over a lamp, or upon glowing coals. If several flasks are used at one time, they may be placed in depressions in the periphery of a sheet-metal disk, which are filled with sand, and furnished with clamps for holding the necks of the flasks; or, they are placed upon a movable support, with a gas pipe and burners throwing out lateral flames; or upon *Levol's* gas-heating apparatus. *Matthey* and *Johnson's*[2] new platinum apparatus permits of many rolls (10 to 100) being boiled at one time in small thimble-like crucibles, which are immersed in the acid. It may be highly recommended on account of its great convenience and cleanliness, and saving of acid. *Tookey*[3] uses a platinum tube for heating.)

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[1] Polyt. Ctrbl. 1857, p. 314. B. u. h. Ztg. 1861, p. 407.

[2] B. u. h. Ztg. 1870, p. 325.

[3] Dingler, cxcvii. 93. B. u. h, Ztg. 1870, p. 283.

By dissolving silver in nitric acid, nitrous acid is formed which does not attack the gold as long as silver is present. But it will do so if it is developed after the silver has been removed. Such development may be caused by the action of the splinter of wood-charcoal placed in the flask to prevent bumping during ebullition, in case it should contain any woody substance. For this reason, it is best to avoid the use of charcoal for this purpose.

g. Washing (rinsing off) the rolls.—After the last boiling with nitric acid, the acid is poured off, and hot distilled water is allowed to flow slowly into the flask from a copper kettle, the spout of which is introduced into the neck of the flask, or, what is still better, from a glass pitcher. While the water is running into the flask the latter should be constantly turned, until it is about ⅔ full of water. The water is then poured out, and this operation is twice repeated, until the last traces of silver nitrate are removed from the roll and the sides of the flask. The flask is now filled entirely full, a small crucible glazed inside, or a porcelain cup or saucer, is placed over its mouth, and both cup and matrass in this position are slowly inverted, which causes the roll to gradually slide down into the cup or crucible. The flask is then drawn away over the edge of the crucible, after which the water, now no longer showing a silver reaction with hydrochloric acid, is poured from the crucible.

h. Drying and annealing of the rolls.—They are thoroughly dried in crucibles, which are covered and placed on the shelf in front of the muffle, or into the round holes of a metal plate, into which they fit. The feet of this plate stand upon a sheet-metal plate, heated by glowing coals from below. The matt lustre rolls, which are of a brownish color and porous, are now heated in the same crucibles in the muffle-furnace at a white heat, whereby they must assume the lustre and color of gold, after which they are taken from the crucibles.

i. Weighing of the rolls.—After the rolls have become cool, they must be quickly weighed, as they easily absorb gases. A roll, and another from a control assay are laid on the opposite pans of a balance. If they agree (in assays from the upper and lower side of a bar, differences may occur), they are both weighed, and the percentage of gold is thus determined. The average is taken of the upper and lower assay. (It is customary to give the lowest percentage of fine assays of silver, p. 149.)

A loss of gold occurs in cupelling, partly on account of the volatilization of gold with other metals and partly by absorption by the cupel (Kapellenzug). According to *Kandelhard* this loss is equalized by the retention of a residue of silver in the roll, but this, according to Rössler,[1] is not always the case, as differences may occur between the found and actual percentage of gold, from a cooler or hotter "brightening" and in alloys of different proportions. According to *Kandelhard's* method, the residue of silver in the roll is 1 thousandth when 2½ parts of silver to 1 part gold have been used in the quartation, and the alloy has been boiled three times, 1.5 to 2.5 thousandths if boiled not quite so thoroughly, and up to 5 thousandths if boiled but once. According to *Rössler* the loss of gold by cupelling increases with the quantity of lead used (when ¼ gramme (3.85 grains) of gold is cupelled with 1 to 2 grammes (15.43 to 30.87 grains) of lead, the loss is only fractions of a thousandth; when 4 to 8 grammes (61.73 to 123.5 grains) of lead are used, it is over 2 thousandths, even if a residue of silver of nearly 1 thousandth is taken into consideration). The loss is also greater the smaller the gold button is (therefore also when a smaller quantity of the sample is weighed) and the smaller the quantity of silver (according to *Rössler*, 1 to 3 thousandths of pure gold are lost if 4 times the quantity of lead is used in the quartating cupellation; if the button contains more than $2\frac{1}{2}$ times the quantity of silver, the residue of silver commences to preponderate, and with a large quantity of silver it seems to be almost in excess). According to this, assays with a small percentage of gold cupelled with much lead would, under otherwise equal conditions, come out somewhat worse than those with a high percentage, and, if loss of gold and residue of silver equalize each other, the loss would preponderate in all smaller assays.

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[1] Dingler, ccvi. 185. B. u. h. Ztg. 1873, p. 26.

An English commission[1] having caused an examination to be made of samples of different coins with an accurately determined percentage of gold, the errors in the assay were found to amount to from $\frac{1}{10000}$ to $\frac{2}{10000}$ per cent.

Platinum renders the surface of the auriferous silver button, after it has been cupelled, crystalline, porous, and rough, and, if much of it is present, gray. It is removed by cupelling the button resulting from quartation, after it has been weighed, with 8 times the quantity of silver and lead, and treating the resulting button, after it has been laminated, with nitric acid until the weight of the roll remains constant and platinum is no longer dissolved with the silver.[2] *Rhodium* and *iridium* produce black stains upon the auriferous silver buttons after the brightening, and, if a large percentage of iridium is present, the rolls break and black iridium powder will be found between the gold. The gold is then dissolved in aqua regia and precipitated with ferrous sulphate.

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[1] Report of the British Association, 1875, p. 127.

[2] Winkler, Löslichkeit von Platinsilber in Salpetersäure in Fresenius' Ztschr. 1874, p. 369. B. u. h. Ztg. 1845, p. 145.

D'Hennin[1] claims to separate the iridium by fusing 12.5 grammes (192.89 grains) of gold containing it with 3 grammes (46.30 grains) of sodium arsenate, 18 grammes (277.78 grains) of black flux, and 20 grammes (308.65 grains) of a flux consisting of a mixture of borax, argol, litharge, and charcoal, into a speiss containing iron and arsenic, while the gold and silver are collected in the lead.

Palladium passes with the silver into solution, if the gold containing it is alloyed with 3 times the quantity of silver.

II. *Pulverulent assay* (*Staubprobe*) *of auriferous silver.* —*a.* A sample, about 5 grammes (77.16 grains), is taken on opposite ends from the upper and lower side of a bar. Duplicates of the sample of 0.5 gramme (7.71 grains) are weighed out, and cupelled in the mint furnace with 8 times the quantity of silver (p. 166) and the quantity of lead which is found to be necessary according to Table II. p. 169, after a preliminary assay has been made. The resulting button is laminated by hammering or passing it between rollers. It is then placed in a flask, the neck of which should not be wider than 6 to 8 millimeters (0.23 to 0.31 inch). Here it is boiled with nitric acid, of 1.2 specific gravity if the percentage of gold is small, and of 1.3 specific gravity if the percentage is larger, for instance 100 thousandths, until the vapors of nitrous acid have disappeared. The bumping is prevented by throwing a carbonized grain of pepper, etc. (p. 172) into the flask. The pulverulent gold is allowed to settle in the flask, which has been placed in a revolving stand. The acid is then poured off into a porcelain saucer or cup, and the gold is rinsed three times with hot distilled water. The flask is now filled with water and inverted in a small unglazed porcelain crucible. In this position they are placed upon the revolving stand until the gold has descended into the crucible. When this is the case, the matrass[1] is carefully drawn away over the side of the crucible. The water is now poured out of the crucible by allowing it to run down on a small rod, and that which remains behind is soaked up with filter-paper. The gold is then dried and strongly ignited in the crucible so that the particles of gold form a coherent mass. It is then weighed.

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[1] Dingler, cxxxvii. 443.

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If the button in brightening is less white, and does not "spit," or if, as is the case where platinum is present, it is crystalline, grayish, and has flat edges, the gold is again cupelled with 8 times the quantity of silver and 3 times that of lead and boiled with acid, and these operations must be repeated until the weight of the pulverulent gold remains constant.

The gold may also be determined in connection with Volhard's assay of silver with potassium sulpho-cyanide (p. 156). Jüptner[2] fuses alloys of gold and silver rich in gold, with 5 to 8 times the quantity of zinc, and dissolves the alloy in nitric acid, whereby the gold remains behind.

b. Separation of auriferous silver grains from samples of ores.—This is done in the manner indicated on pp. 164 *et seq.*

B. Alloys of gold with copper.—The metals are separated by cupelling the alloy with 32 times the quantity of lead, and adding 3 times the quantity of silver, otherwise the process is the same as given on p. 169.

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[1] The narrow neck of the flasks used in the assay of gold prevents the air from entering while the flask is being removed, which otherwise might stir up the gold dust.

[2] Fresenius' Ztschr. 1879, p. 104; B. u. h. Ztg. 1879, p. 187.

V. PLATINUM.

36. ORES.

Native platinum, almost always combined with other metals of the platinum group (Rh, Ir, Pd, Os), with precious (Au) and base metals (Fe, Cu), and admixed with iridosmium, earthy and metallic minerals.

37. ASSAY OF PLATINIFEROUS ORES.

A. Fire assays.[1]—These extend to the determination of—

1. *Percentage of sand.*—2 grammes (30.87 grains) of ore are mixed with 10 grammes (154.32 grains) of granulated silver and placed in a clay crucible glazed with fused borax. It is covered with 10 grammes (154.32 grains) of borax glass, with a small piece of wood charcoal, and fused. The resulting button is weighed, and its difference in weight, as compared with that of the ore, giving due consideration to the added silver, indicates the percentage of sand.

2. *Percentage of gold.*—10 grammes (154.32 grains) of the ore are boiled with mercury for several hours. It is then washed out with hot mercury, and the gold amalgam distilled in a small retort.

3. *Percentage of platinum.*—The platinum is combined with lead by fusing 50 grammes (771.61 grains) of ore with 75 grammes (1157.42 grains) of granulated lead, 50 grammes (771.61 grains) of galena, 10 to 15 grammes (154.32 to 231.48 grains) of borax, and adding to the fused mass 50 grammes (771.61 grains) of litharge;

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[1] Muspratt's Chem., v. 1151.

or 20 grammes (308.65 grains) of ore are fused with 15 grammes (231.48 grains) of borax, 30 grammes (462.97 grains) of soda, 1 gramme (15.43 grains) of powdered charcoal, and 50 grammes (771.61 grains) of litharge. The fused mass is allowed to cool off, and the lead button separated from matt (sulphur compounds of copper, iron, and lead) above it, and the iridosmium below it. The lead button, if too large, is scorified with some borax (p. 65), and cupelled at as high a temperature as possible. The platinum remaining is purified by a further fusion with 6 to 7 per cent. of lead in a lime crucible heated with illuminating gas and oxygen.

B. Wet assay.—5 to 10 grammes (77.16 to 154.32 grains) of ore are treated with hydrochloric acid, and the residue is washed out and digested with *aqua regia* for from 8 to 12 hours. The platiniferous solution is filtered from the residue (sand, iridosmium) and evaporated almost to dryness. Absolute alcohol and solution of salamoniac are then added. This is again filtered and washed, and the yellow ammonio-platinic chloride is dried. This is highly heated, and the resulting spongy platinum is weighed. If the ore contains gold, it is precipitated from the filtrate of ammonio-platinic chloride with ferrous sulphate. The precipitated gold is then digested with hydrochloric acid, filtered, washed and dried, and fused with the addition of some borax glass.

38. ALLOYS OF PLATINUM.

These may be:—

1. *Gold with platinum.*—The alloy is cupelled with three times the quantity of silver, and sufficient lead to remove any copper which may be present (8 to 30 times the quantity of lead if from 200 to 500 thousandths or

more of copper are present). The laminated button is treated with nitric acid, as in the gold assay (p. 169), whereby the platinum will be dissolved with the silver, the gold remaining behind. The silver is precipitated from the solution by means of common salt, and the platinum is separated from the filtrate as ammonio-platinic chloride, and further treated as on p. 180. If the percentage of gold is large, the alloy is dissolved in *aqua regia*, and the separation conducted in the manner indicated for platinum ores (p. 180).

2. *Silver with platinum.*—0.5 gramme (7.71 grains) of the alloy are cupelled with a sufficient quantity of lead to remove the copper which may be present, and with such a quantity of silver (to be determined by a preliminary assay) as to make the ratio, 1 part platinum to 2 parts of silver. The alloy is laminated and boiled twice (each time from 10 to 12 minutes) with concentrated sulphuric acid of 1.85 specific gravity, whereby platinum will remain behind in the form of a small roll, and, if a larger quantity of silver is present, as a powder. It is then washed with hot water, dried, ignited, and weighed.

3. *Silver and gold with platinum.*—200 milligrammes (3.08 grains) are cupelled with sufficient silver, for instance, 100 milligrammes (1.54 grains), to make the ratio 1 part gold to 3 parts silver, and with lead to remove the *base metals*. The button is laminated, being frequently heated during the operation. It is then made into a roll and boiled with concentrated sulphuric acid. The residue is washed, ignited, and weighed; the difference in weight represents the *silver* originally present plus that added to it. The residue, containing gold, platinum, and iridosmium, is cupelled with lead, and with a quantity of silver at least 12 times that of the platinum

(the effect of less silver would be to leave a residue of platinum, and if more is taken the residue will be pulverulent instead of in the form of a roll). The roll is first boiled with nitric acid of 1.16 specific gravity, and then with acid of 1.26 specific gravity, after which the residuum (gold and iridosmium) is washed and ignited. The dissolved platinum is determined from the difference. The residue is digested with *aqua regia*, and the gold precipitated with ferrous sulphate, while iridosmium remains behind. About 3 hours are required for two assays.

VI. NICKEL.

39. ORES.

Copper nickel, $NiAs$, with 44 Ni; *antimonial nickel* (*breithauptite*), $NiSb$, with 31.4 Ni; *rammelsbergite*, $NiAs_2$, with 28.2 Ni; *nickel sulphide* (*millerite*), NiS, with 64.5 Ni; *antimonial nickel ore* (*ullmannite*), $NiSbS$, with 27.6 Ni; *nickel glance* (*gersdorffite*), $NiAsS$, with 35.1 Ni; *nickel silicates* as *revdanskite* and *garnierite*, with 10 to 20 Ni; *nickel arseniate*, $Ni_3As_2O_8+8H_2O$, with 29.5 Ni; *nickeliferous iron*, *copper*, and *magnetic pyrites*.

40. FIRE ASSAY (*Plattner's assay*).

This is based upon the formation of constant combinations of Ni_2As, and Co_2As, with respectively 60.7 Ni and 61.1 Co, and their subsequent treatment, in a manner to be indicated with borax, after other foreign admixtures have been removed. The process requires certain modifications if *copper*, *lead*, *bismuth*, and *antimony* are present.

A. Compounds free from copper.

1. A sufficient quantity of assay sample is weighed out so that the resulting buttons of Ni_2As and Co_2As will weigh from 0.4 to 0.6 gramme (6.17 to 9.26 grains). Thus, about 5 grammes (77.16 grains) of poor ores will be required, 1.5 to 2.5 grammes (23.15 to 38.58 grains) of medium, and 0.5 to 0.6 gramme (7.71 to 9.26 grains) of rich ores.

2. Compounds containing *metallic sulphides* must be *completely roasted* with charcoal and ammonium carbonate; otherwise, the buttons cannot be properly slagged with borax. Substances free from sulphur need not to be roasted.

5 grammes (77.16 grains) of ore containing sulphates which cannot be decomposed by roasting (gypsum, barytes, etc.), with 10 to 15 grammes (154.32 to 231.48 grains) of borax, 5 to 10 grammes (77.16 to 154.32 grains) of glass, and 0.5 gramme (7.71 grains) of resin are placed in a suitable crucible (Fig. 42, p. 67), covered with a layer of common salt, and fused to (brittle) matt (p. 104). This is dead-roasted. 0.5 to 1.5 gramme (7.71 to 23.15 grains) of arsenic are added if the nickel was not combined with sulphur or arsenic.

3. *Arsenizing.*—The roasted assay sample is intimately rubbed together with 1 to 1½ times the quantity of metallic arsenic in an iron mortar, placed in a suitable covered crucible (Fig. 42, p. 67), and heated in the muffle, kept at orange-red heat (for 10 to 15 minutes) until the arsenical flame and vapors have ceased to appear. When this is the case, the metallic oxides contained in the roasted sample will have been reduced by a part of the arsenic, and converted by another part into metallic arsenides of variable composition (of iron, nickel, cobalt, etc.), which are either only sintered together (especially if the charge is rich in cobalt), or fused.

Compounds free from sulphur and rich in arsenic, containing more arsenic than is necessary for the formation of Co_2As and Ni_2As, do not require roasting and arsenizing. Alloys (argentan, nickel coins, nickeliferous black copper, etc.) must be laminated, and several times arsenized with an equal quantity of arsenic; and also substances rich in cobalt (for instance, mixtures of nickel and cobalt oxides), which may have been precipitated in the wet way.

4. *Reducing and solvent fusion* for the purpose of collecting the metallic arsenides into a button (arsenical iron, arsenical nickel, arsenical cobalt), and of slagging off earths and foreign oxides, zinc being entirely, and antimony partly volatilized in the operation. The mass is placed in a sound crucible, and 10 to 12.5 grammes (154.32 to 192.90 grains) of potassium carbonate and flour are added to it. Upon this come a small spoonful of borax and two of powdered glass, and a covering of common salt with a small piece of coal. The crucible is then placed in the muffle-furnace, wood-charcoal is piled high around it, the mouth of the muffle is closed, and the charge, after the "flaming" has ceased, is fused for one-half to three-quarters of an hour at an orange-red heat. The assay is then taken out, allowed to cool off, and the brittle button very carefully freed from slag.

Modifications which may occur:

a. Addition of iron filings: 0.5 to 0.75 gramme (7.71 to 11.57 grains) of iron filings must be added during arsenizing, if the ores, etc., are rich in cobalt, and refractory; 0.05 to 0.20 gramme (0.77 to 3.08 grains), if they are entirely free from iron, or contain but little of it, in order to prevent the slagging off of cobalt too soon, by the borax. If *lead* is present, 0.5 to 0.75 gramme (7.71 to 11.57 grains) of iron in the form of a thick wire are added, or the mass is fused in an iron crucible, which will allow a better regulation of the consumption of iron. The lead attaches itself upon the button of arsenides, and its weight is found by weighing lead and button together, cutting the former off and reweighing. If *bismuth* is present, it would attach itself upon the brittle button of arsenides, in the form of brittle metal, which could not be detached from it. In this case, it is necessary to add 0.5 to 0.6 gramme (7.71 to 9.26 grains) of granulated lead to the charge, when a ductile alloy of both metals will separate on the button of arsenides, which can be easily disconnected from it. The approximate percentage of bismuth can be calculated after deducting the added granulated lead, minus 4 per cent. loss.

b. Arsenizing and fusing in one operation.—The roasted assay sample is rubbed together with arsenic in the same manner as previously stated, and the mixture is wrapped up in a cylinder of soda paper. The cylinder is formed over a wooden stick of 16 millimeters (0.63 inch) diameter, by closing the lapping edges with lac. It is pressed firmly into a crucible (Fig. 42, p. 64) and covered with 15 grammes (231.48 grains) of black flux, 1 small spoonful of borax, 1 small spoonful of glass, 15 grammes (231.48 grains) of common salt, and a small piece of charcoal. Accurate results are obtained by this process.—Or, the roasted sample is rubbed together with an equal quantity of arsenic and 15 per cent. of arsenical iron (Fe_2As), and fused with the above fluxes.

5. *Slagging off of the arsenical iron.*—Wood charcoal is placed all about the inside of the muffle, and one or two refining dishes are placed in the centre of it. The muffle is then closed, and the dishes are brought to a white heat by a strong fire. 1.5 to 2 grammes (23.15 to 30.87 grains) of borax glass are then placed in the dishes by means of an iron spoon (or wrapped up in a cornet), the muffle is closed and the borax fused. The button of arsenides is now placed in the dish, the mouth of the muffle is again closed, and the button fused *as quickly as possible* at a *very high* temperature (if the temperature is too low and the fusing takes too much time, cobalt also will be slagged off). The mouth of the muffle is now opened, placing a piece of glowing charcoal in front, to allow the entrance of air, whereby the arsenide of iron is oxidized to basic iron arseniate. This covers the button with a crust or scale (the scaling of the button) which is continuously dissolved by the borax until the

surface of the dull button appears bright, when this operation is finished. The dish is lifted out by means of the tongs, and the lower part of it is first dipped into water until its contents has ceased to glow, when the entire dish is submerged. The following are indications of a successful assay: The button is bright, the slag black or green, with a bluish tint, which is a sure indication of all the iron having been removed.

Modifications.—If the button is very rich in iron it is repeatedly treated with fresh borax, as this is saturated and becomes stiff and the button no longer "drives."

Separation of *copper-red scales* of iron arseniate from strongly saturated borax. *More cobalt* will slag off (the slag has a strong blue tint) if the temperature is too low or the slagging off is continued too long, or when no iron, or but little of it, was present in the button.

6. *Dearsenizing.*—An excess of arsenic is volatilized by heating the button in a small covered crucible (Fig. 39, p. 66) in charcoal powder, in the muffle heated to bright redness for one-fourth to one-half hour, in order that constant combinations of Ni_2As and Co_2As shall be formed. The resulting button is weighed, and the operation is repeated until its weight remains constant.

7. *Slagging off the cobalt arsenide.*—The process is the same as in slagging off the iron arsenide (p. 185), but at a higher temperature, the quiet button remaining *bright* during the slagging off of the cobalt. The process is interrupted as soon as a film of apple-green basic nickel arseniate forms on the surface of the button. The dish is taken and cooled off in the same manner as in the slagging off of iron arsenide (p. 185). If the assay has been properly done, the bright, white button will show on its surface small green patches of nickel arseniate, the slag is blue with a violet tint (from the blue of the cobalt and the brown of the nickel), and a green stain will be per-

ceptible on the place where the button has rested. The button consisting of Ni_2As is weighed, and the percentage of nickel calculated therefrom (p. 182), the Co_2As being determined from the difference of $Co_2As + Ni_2As_2$.

B. Cupriferous compounds.

A percentage of copper[1] remains behind with Ni_2As as a constant combination of Cu_3As, and can be determined according to *Plattner's* method:

1. *If the percentage of copper is small*, and does not exceed that of nickel, by the addition to the weighed button ($Ni_2As + Cu_3As$) of 6 to 8 times the quantity of gold accurately weighed (to prevent a slagging off of the copper in the subsequent operation). The arsenide button with gold addition wrapped in a cornet is placed in salt of phosphorus which has been fused in a suitable shallow dish. This salt exerts a more vigorous effect than borax in slagging off with yellowish-brown color the nickel arseniate which will be formed. If necessary, the oxidizing process is continued by renewing the saturated salt of phosphorus until the button appears bright, a proof that the nickel is slagged off, the complete volatilization of the arsenic being indicated later on by the button ceasing to fume. The remaining alloy of Au and Cu is weighed, and the weight of the copper, which is obtained by deducting that of the added gold, is calculated to Cu_3As, with 71.7 per cent. Cu, and deducted from the total weight of the $Ni_2As + Cu_3As$, from which the percentage of nickel is calculated.

This assay becomes less accurate with an increase in the percentage of copper, as, during the slagging off of the last portions of the nickel arseniate, the copper also commences to slag off. For this reason—

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[1] B. u. h. Ztg. 1868, p. 24; 1868, p. 94 (Kleinschmidt); 1878, p. 88 (Schweder).

2. The *wet method* is partially made use of when the *percentage of copper is large.* The processes are as follows:—

a. The button consisting of Ni_2As and Cu_3As is dissolved in nitric acid, and evaporated to dryness with sulphuric acid. The residue is digested with aqueous sulphurous acid until no odor of the latter remains. The copper and arsenic (also antimony) are now precipitated from acid solution by sulphuretted hydrogen, and the arsenic sulphide (also antimony sulphide) is extracted with a warm solution of sodium sulphide. The residue remaining in the filter is washed and dried in the roasting dish in front of the muffle, and is then ignited. The copper sulphate is rubbed up and strongly heated, ammonium carbonate being added towards the end. The copper oxide which has been produced is weighed, and calculated to Cu_3As. This is deducted from Ni_2As+Cu_3As to determine the Ni_2As (*Patera*).

b. By another method, the ore, etc., is dissolved, and the copper precipitated by the galvanic current (pp. 115 *et seq.*), and the remaining solution with potassium hydrate. The precipitate, containing iron, nickel, and cobalt, is washed, dried, ignited, arsenized, and the further process conducted as given in the dry method, p. 183. When *much iron* is present, it is better, on account of the labor of washing the iron precipitate, to prepare an assay according to Plattner, for Ni_2As+Cu_3As, to separate the copper from a second fresh charge by electrolysis, to calculate the copper to Cu_3As, and deduct this from Ni_2As+Cu_3As, which will give the Ni_2As (Schweder).

Nickeliferous pyrrhotine, with 0.82 per cent. Cu and 1.72 per cent. Ni and Co: 2 grammes (30.87 grains) are dissolved as above, p. 117, and the copper is precipitated by electrolysis from a solution of 40 cubic centimeters (2.44 cubic inches) of nitric acid, and 360 cubic centimeters (21.96 cubic inches) of water (p. 115); or 5 grammes (77.16 grains) of ore are roasted and charged with arsenic in a soda paper cylinder (p. 185), and fused with fluxing agents in the crucible (p. 186); the iron is slagged off twice and the button then dearsenized. If cobalt is absent, Ni_2As+Cu_3As will remain behind, and the nickel is then calculated as previously stated (p. 187). Cobalt and nickel may also be determined by electrolysis, and caculated to $(Ni,Co)_2As$, and the Cu_2As determined from the difference.

c. Compounds difficultly soluble, as, for instance, slags.—These are roasted, arsenized, and fused according to the process given on p. 183. If they are poor in nickel, several buttons (say five) are wrapped in a cornet and treated with borax, as before described. The iron is slagged off, the excess of arsenic removed, and the button (Ni_2As+Cu_3As) weighed. It is then dissolved in 20 cubic centimeters (1.22 cubic inches) of nitric acid, 200 cubic centimeters (12.2 cubic inches) of water are added, and the copper is precipitated by electrolysis until it commences to be colored black by the arsenic (p. 118). The Cu_3As is calculated from the precipitated copper, and deducted from the Ni_2As+Cu_3As, etc., or, what is still better, in order to avoid constantly watching the precipitation of copper, lest arsenic be precipitated with it, the button of Ni_2As+Cu_3As is dissolved in nitric acid, in a covered beaker-glass, then evaporated to dryness, and the copper and arsenic are precipitated with sulphuretted hydrogen. The filtrate is heated in order to drive off the sulphuretted hydrogen, ammonium sulphate and ammonia are added, and the nickel determined by electrolysis (see later on). This is calculated to Ni_2As, which is deducted from $NiAs+Cu_3As$, and Cu_3As is found from the difference.

C. Compounds containing antimony.

If a large amount of antimony is present, it becomes necessary to remove it from the dissolved ore by sulphuretted hydrogen. It is then filtered, and the filtrate boiled in order to expel the sulphuretted hydrogen. The filtrate is now oxidized with potassium chlorate, the iron, nickel, and cobalt are precipitated with potassium hydrate, and the precipitate is filtered, dried, ignited, and arsenized (p. 183).

41. WET ASSAY.

The *gravimetric* analysis, being more accurate, and, especially the electrolytic assay, more simple than the *volumetric analysis*, it is more frequently used for the wet assay of nickel.

A. Gravimetric assay.

1. *Electrolytic assay.*[1]—This is based upon the precipitation of nickel (and at the same time, of cobalt, if present) from ammoniacal solution (copper from acid solution) by the galvanic current. When *copper* and *lead* are present, 1 gramme (15.43 grains) of ore is dissolved in 20 cubic centimeters (1.22 cubic inches) of nitric acid, and evaporated with a few drops of sulphuric acid in order to form lead sulphate, and the copper, antimony, and arsenic in acid solution are precipitated with sulphuretted hydrogen. (This method of precipitation is to be preferred as, if the copper is previously precipitated from acid solution by the galvanic current, antimony and arsenic remain in the filtrate.)

The filtrate is evaporated in a porcelain dish, first over the lamp, then on the water-bath, with the addition of a few drops of nitric acid; and, in case dust should float in the fluid, some hydrochloric acid is also added, when the liberated chlorine will destroy the organic substances which otherwise, being converted into sugar by sulphuric acid, would, in the subsequent precipitation of the iron, hold a part of it in solution as ferrous oxide, which would then be precipitated with the nickel. The free sulphuric acid is expelled by heating the sand-bath. The mass is next dissolved in water and supersaturated with ammonia, in order to prepare an ammoniacal solution of copper.

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[1] Fresenius' Ztschr. 1878, p. 1; B. u. h. Ztg. 1877, p. 5 (Schweder).

If but little iron is present, ammonia may be used directly; but should there be a larger quantity, the precipitated ferric hydrate remains nickeliferous. If this is the case, the residue, *completely* freed from *free* sulphuric acid by evaporation, is dissolved in 100 cubic centimeters (6.1 cubic inches) of hot water, and after the solution has become entirely cold, 200 to 300 cubic centimeters (12.2 to 18.3 cubic inches) of cold water are added, according as less or more iron is present. Next a solution of ammonium sesquicarbonate in 12 parts of water is added drop by drop from a pipette, under constant stirring, until the liquid appears dark brown, but without being turbid (if this is the case, a few drops of sulphuric acid must be added), and without developing carbonic acid. The vessel is then covered with a watch crystal, and the liquid *slowly* heated to the boiling point, whereby the greatest part of the iron will be separated as basic sulphate of a leather-yellow color. The vessel is taken from the fire, the watch-crystal rinsed off, and the liquid placed in the water-bath and allowed to settle. It is then filtered, and the precipitate, which is free from cobalt and nickel, washed with hot water. If the assay sample is rich in iron, the filtrate will still contain Fe. In this case it is allowed to become quite cold, and is then again precipitated with ammonium carbonate, as above, etc., but the filtrate will always contain notable traces of iron. A *few* drops of ammonium acetate are then added, and the filtrate is evaporated so far that the solution will be contained in the beaker-glass, in which it is intended to make the electrolytic precipitation. The fluid is then filtered into this beaker from the small quantity of iron sediment, supersaturated with ammonia, etc.

Instead of supersaturating the solution with ammonia, it is better to add 20 cubic centimeters (1.22 cubic inches) of ammonia and the same quantity of ammonium sulphate and to electrolyze it in the apparatus used for the galvanic assay of copper (p. 115). The binding screws of the electrode should be well coated with shellac to protect them against corrosion by the ammoniacal vapors.

In the presence of much iron, and of ammonium chloride, chlorine which attacks the platinum, will be developed on the positive electrode. For this reason a sulphuric acid solution is to be preferred, and ammonium sulphate exerts a favorable effect upon the process.

As the ammoniacal nickel solutions offer greater *resistance* to the galvanic current than the acid copper solutions, the nickel will be principally deposited on the inner sides and lower end of the platinum cone, where small bubbles of hydrogen may also make their appearance, causing the nickel to be deposited in fine, non-coherent laminæ, which spring off in the subsequent rinsing and drying, thus occasioning losses. This must be avoided by suspending the platinum cone in such a manner that its lower edge shall be about 1.5 centimeters (0.59 inch) above the bottom of the glass; further, by increasing the electrical conductivity of the solution by an addition of ammonium sulphate, and by using a current sufficiently strong to give at least 100 cubic centimeters (6.1 cubic inches) of oxyhydrogen gas in the voltameter in half an hour. A black coating of nickel sesquioxide, which may be formed on the positive electrode, will generally disappear by strongly supersaturating the fluid with ammonia. Should this not produce the desired effect, the platinum cone is first taken out, placed in water, the spiral is then removed, and a few drops of hydrochloric acid are allowed to drip down on it, which will cause the coating to dissolve with evolution of chlorine. Some ammonia is then added and the apparatus again put in place and allowed to operate for a few hours longer. Should ferric hydrate be separated, it is collected, in case it is to be determined by volumetric assay, and added to that first obtained.

After an electrolyzation of about 18 hours, the platinum cone is taken out, placed in a beaker-glass containing water, and rinsed off with hot water. It is then taken out and placed upon several thicknesses of filter paper. From here it is brought into a beaker-glass containing alcohol, alcohol being likewise allowed to run down on the wire. The cone is next placed upon blotting paper and then completely dried upon a sheet-iron plate heated over a lamp. After it has become cool, it is weighed and the nickel (or nickel and cobalt) is ascertained from the increase in weight.

When *zinc* is present, some of which is precipitated along with nickel (hydrochloric and nitric acid, and their salts, prevent this precipitation, but sulphuric acid does not), the hydrochloric or nitric acid solution is treated, after driving off the sulphuretted hydrogen, with sodium carbonate until it exhibits only a slight acid reaction. More sulphuretted hydrogen is then introduced, in order to precipitate zinc sulphide, until no further increase of the precipitate is perceptible; a drop of a diluted solution of sodium acetate is then added. Sulphuretted hydrogen is now again introduced for some time, and the liquid then allowed to stand quietly for twelve hours. It is then filtered and washed with sulphuretted hydrogen water. The zinc sulphide is dissolved in hydrochloric acid, and precipitated, after the sulphuretted hydrogen has been expelled, by sodium carbonate; or the zinc sulphide, with the addition of some sulphur, is ignited in a current of hydrogen gas (p. 121). The nickeliferous filtrate, from the precipitate with sulphuretted hydrogen, is heated, some ammonia added, and it is then electrolyzed, after the iron has been separated in the manner indicated on p. 191.

The platinum cone coated with cobalt and nickel is placed in a beaker-glass, and covered with a mixture of 1 part of nitric acid, of 1.2 specific gravity, and 3 parts of water. This is heated until solution of the metallic deposit is complete. The cone is then taken out and rinsed off with hot water. The solution is evaporated to a small volume, and some potassium hydrate added until precipitation just begins. The precipitate is dissolved by the addition of some acetic acid, a concentrated solution of potassium nitrite is added, and the fluid allowed to stand for 24 hours. The yellow precipitate of $CO(NO_2)_3 + 3KNO_2$ is filtered off, and washed first with potassium acetate and then with alcohol. It is next dissolved in sulphuric acid, and digested till the odor of nitrous acid has been entirely dispelled. It is then neutralized with ammonia. 20 cubic centimeters (1.22 cubic inches) of ammonium sulphate and the same quantity of ammonia are added, and the solution again subjected to electrolyzation. The cobalt is weighed, and the nickel determined from the difference.

Determination of nickel in pyrites and matt.[1]—2 to 5 grammes (30.87 to 77.16 grains) of the substance are dissolved in hydrochloric acid, to which some nitric acid has been added, and the solution precipitated with sulphuretted hydrogen (p. 190). The filtrate is boiled in order to expel the sulphuretted hydrogen, and nitric acid or potassium chlorate is added to oxidize ferrous to ferric oxide. Ammonia is then added until some precipitate forms, but without precipitation being complete. Some acetic acid is now added until a deep-red solution is formed. This is boiled, and a solution of concentrated sodium phosphate is added *in excess.* The precipitate of iron is filtered off and washed with hot water containing some acetic acid. The filtrate is boiled, and potassium hydrate added until an odor of ammonia is clearly perceptible. The apple-green nickel phosphate is washed out, dissolved in diluted sulphuric acid, and made strongly alkaline by addition of ammonia. The solution is then subjected to electrolyzation. When more than 3 per cent. of nickel is present, the precipitate of iron is again dissolved, reprecipitated, etc. A trace of iron, but not enough to influence the precipitation of nickel by the battery, may remain in the solution if too small a quantity of sodium phosphate is present, or if the solution was made alkaline before the addition of acetic acid.

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[1] B. u. h. Ztg. 1878, p. 41.

2. *Other assays.*[1]

a. The ore, etc., is dissolved in *aqua regia* and evaporated with the addition of sulphuric acid. Aqueous sulphurous acid is added to this in order to reduce the arsenic acid. The sulphurous acid is then removed by boiling, and the copper, arsenic, etc., are precipitated with sulphuretted hydrogen. The liquid is then filtered, the sulphuretted hydrogen removed by evaporation, and the ferrous oxide oxidized by potassium chlorate. Sodium carbonate boiling hot, is then added until a permanent precipitate is formed. A drop of hydrochloric acid is now added, until the precipitate just disappears, and then a large quantity of sodium acetate added to the hot solution. This is boiled for 10 to 15 minutes, and the precipitate of iron and alumina quickly filtered off, washed, and again dissolved in hydrochloric acid, etc., in order to separate such traces of nickel as it may contain. Chlorine water is added to the nickeliferous filtrate, followed by potassium hydrate (some zinc also will be precipitated), and if necessary, more chlorine water. This is boiled for a quarter of an hour, or until the precipitate of nickel and cobalt sesquioxides has assumed a black color. It is then filtered, the precipitate dried, and the oxides reduced in a current of hydrogen gas (p. 121). For *the separation of nickel and cobalt*, the weighed metals are dissolved in hydrochloric acid. The solution is slightly supersaturated with sodium carbonate. A concentrated solution of potassium nitrite is added, and then some acetic acid until a weak acid reaction is established. The liquid is then allowed to stand for 24 hours, when the yellow cobalt precipate is filtered off and washed with a concentrated solution of potassium chloride or potassium sulphate. The precipitate is now dissolved in hydrochloric acid, the solution precipitated with sodium hydrate and chlorine water, etc., and the cobalt sesquioxide reduced in a current of hydrogen gas. The solution carrying the nickel is precipitated with potassium hydrate and chlorine water, etc.

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[1] Fresenius' Verfahren für Erze, Leche und Speisen in Fresenius' Ztschr. xii. 70.

In order to *separate the iron*, the oxidized iron is partly precipitated with sodium carbonate (p. 195). Some acetic acid is added, and the liquid is heated to 30 to 40° C. (86 to 104° F.) in order to dissolve the precipitated iron. It is then boiled, the precipitated iron is again dissolved two or three times, and the precipitation repeated to separate the nickel from it. Finally, by adding sodium sulphide the ferric oxide is converted into iron sulphide, and this is treated with diluted hydrochloric acid, whereby a trace of nickel sulphide may still be found in the residue.

b. Nickeliferous solution from the assay with sulpho-cyanide for determining copper in nickel coins.—In order to decompose the sulpho-cyanide, the solution is evaporated with the addition of 10 cubic centimeters (0.61 cubic inch) of nitric acid, which will cause the fluid to become first red, and then colorless. The nickel is precipitated by pouring the nickeliferous liquid into a boiling solution of 100 cubic centimeters (6.1 cubic inches) of sodium hydrate, 10 per cent. strength, which is boiling in a platinum evaporating dish. It is allowed to boil, then diluted with water, and again heated to the boiling point. It is allowed to settle, and then decanted through a filter. The precipitate is again boiled three times, each time with 200 cubic centimeters (12.2 cubic inches) of water, and then filtered. The precipitate is dried, heated to redness, and rubbed fine, again washed with boiling water, dried, ignited, and the nickel determined from the nickel protoxide[1] (now free from alkali) with 78.38 per cent. nickel.

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[1] Fresenius' Ztschr. 1878, p. 58.

Inaccurate results will follow if less, or less concentrated, sodium hydrate is used, or if the washing is continued too long, as under these circumstances some nickel is dissolved as hydrated oxide.

B. Volumetric assay with sodium sulphide.[1]—The copper which may be present is removed by means of sulphuretted hydrogen, and its percentage determined by the potassium cyanide method (p. 124). The filtrate from the precipitation with sulphuretted hydrogen is evaporated with nitric acid, and the iron precipitated with ammonia. The precipitate is dissolved twice or three times, and again precipitated with ammonia (the methods with ammonium sesquicarbonate (p. 19) or with sodium acetate (p. 195) give a more accurate separation); a standard solution of sodium sulphide, 50 cubic centimeters (3.05 cubic inches) of which precipitate 0 25 gramme (3.85 grains) of nickel, is then added to the vigorously boiling solution, until all the nickel (with cobalt) has been separated. The addition of sodium sulphide is made in quantities of not more than $\frac{1}{4}$ cubic centimeter (0.015 cubic inch) at a time, the solution being maintained at the boiling point, until a filtered drop becomes brown when brought in contact with lead solution upon a porcelain plate.—The solution of lead is prepared by dissolving equal quantities of lead acetate and potassium tartrate in caustic potassa. The normal solution is prepared by dissolving 0.25 gramme (3.85 grains) of pure nickel (or cobalt), or an equivalent quantity of pure oxide or salt, in 5 cubic centimeters (0.3 cubic inch) of concentrated nitric acid. This is diluted with water, supersaturated with ammonia, tested with a saturated solution of sodium sulphide, which is thereupon suitably diluted.

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[1] Journal für prakt. Chemie, lxxxviii. 486 (Küntzel); xcii. 450 (Winkler); Fresenius' Ztschr. vi. 66 (Braun).

Separation of cobalt.—The metallic sulphides of nickel and cobalt, which have been precipitated with sodium sulphide, are filtered off, and the precipitate is washed with sulphuretted hydrogen water. It is then dissolved in *aqua regia* and evaporated with hydrochloric acid to expel the nitric acid. It is now strongly diluted with water in a suitable flask, and nearly neutralized. Elutriated barium carbonate is added, chlorine gas introduced, and the precipitated black cobalt sesquioxide dissolved in hydrochloric acid. The barium is precipitated with sulphuric acid, ammonia in excess is added, and the cobalt titrated with solution of sodium sulphide. The barium is then precipitated from the nickeliferous filtrate, ammonia is added, and the nickel similarly titrated with solution of sodium sulphide. When *zinc and manganese* are present, the ores are fused with potassium cyanide, arsenious acid, soda, and black flux, to a button containing all the nickel and cobalt, as well as a part of the copper and iron, while zinc and manganese are slagged off. The button is dissolved in *aqua regia*, the copper and arsenic are precipitated, hot, with sulphuretted hydrogen, and the nickel and cobalt determined as above.

C. Colorimetric assay.[1]—A colorimetric method for determining nickel has been proposed by Winkler, but it is of little practical value.

VII. COBALT.

42. ORES.

Smaltine, $CoAs_2$, with 28.19 Co; *cobalt glance* (*cobaltine*), $CoAsS$, with 35.5 Co; *cobalt pyrites* (*linnaeite*), ($NiS.CoS.FeS$) ($Ni_2S_3.Co_2S_3.Fe_2S_3$), with 14.6 Ni and 11 to 40.7 Co; *glaucodot*, ($Fe\,Co$) AsS, with 24.77 Co; *earthy cobalt*, $(CoO.CuO)2MnO_2+4H_2O$; *cobalt bloom*, $Co_3As_2O_8+8H_2O$, with 37.5 $CoO = 29.5$ Co.

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[1] Journ. f. prakt. Chem., xcvii. 414.

43. ASSAYS OF COBALT.

The object of the assays is—

1. The *determination of cobalt* by the dry (p. 183) or the wet method; in the latter case by gravimetric (p. 195) and volumetric analysis (p. 197), of which the details have already been given in the foregoing chapter on nickel.

2. The determination *of the blue coloring power* (density), and *the beauty of the colors* (smalt colors) which are formed in fusing ores and products containing cobaltous oxide with different quantities of potassium silicates (*smalt assay*).

44. SMALT ASSAY.

Cobaltous oxide, either contained as such in the ores (earthy cobalt, cobalt bloom), or produced by roasting sulphurized and arsenized ores, gives a blue color to fused potassium silicate (smalt glass, very likely $CoO.3SiO_2 + K_2O.3SiO_2$), the color, under otherwise equal conditions, being the more intense, the richer the ore in cobaltous oxide. The presence of foreign metallic oxides, which also dissolve in potassium silicate, exerts an injurious effect upon the beauty of the blue tint.

Nickel protoxide, the most injurious foreign substance, produces an objectionable reddish or violet tint; *ferrous oxide*, if present in small quantities, gives a greenish shade, but *ferric oxide, bismuth oxide, lead oxide*, and *manganous oxide* effect the cobalt color to a very small extent only. *Manganic oxide* gives a violet tint; *cupric oxide*, a green; *cuprous oxide*, a red tint; while the coloring power of *manganous oxide* is counteracted by that of *ferrous oxide*, if both are present.

In roasting arsenized and sulphurized cobalt ores, the various metals become oxidized in succession, cobalt the soonest of them all, so that it becomes necessary to conduct the roasting of the ores in such a manner that cobaltous oxide only is produced, which, on being fused with silicic acid and potash, gives the beautifully colored smalt. The foreign metals should not become oxidized, but remain combined with arsenic or sulphur, forming a cobalt speiss.

As, in roasting the above-named arsenides and sulphides, cobalt is first oxidized, and iron and bismuth earlier than copper and nickel, *ores containing copper* and *nickel* must not be roasted too strongly, and least of all dead-roasted; this may, however, be done with *entirely pure ores of cobalt*, or such as contain only *iron*, as, in the latter case, ferric oxide is formed, which only slightly affects the cobalt color. If impure ores are *roasted too little*, a beautiful smalt is formed, but much cobalt is lost in the speiss.

The object of the smalt assay is either, *a*, the determination of the coloring power of a sample (*assay for determining the intensity of the color*), or, *b*, to acertain the degree of roasting to which the ore must be subjected in order to obtain a color of pure quality (*assay to determine the color tone*), or, *c*, to determine how much of an already known sample must be taken to produce a certain shade of color.

Several lots of ore, each from 1 to 5 grammes (15.43 to 77.16 grains) according to the richness of the ore, are weighed off. The separate lots are each roasted for a different length of time (for instance, the first lot ¼ of an hour, and the subsequent lots each from 10 to 15 minutes longer), while one of the samples is left unroasted. Each sample is divided by weighing into two equal parts, of which one is tested with fluxes to determine the *quality* of color, and the other its *intensity*.

A. Assay to determine the quality of color.—Each sample is mixed with three times the quantity, by weight, of quartz free from iron and manganese, and with a quantity of pure potash corresponding to half the combined weight of quartz and ore. The mixture is placed in flat dishes of white fire-clay (smalt-dishes). It is then fused in the muffle (Fig. 25, p. 51), which should be heated as strongly as possible, until a completely homogeneous glass has been formed (this will require 4 hours or longer). A sample is then taken from the charge by means of a pair of tongs and cooled off in water. The mass is dried and pounded in a bright steel mortar, in order to obtain angular fragments (powdered smalt is apt to appear dirty). The fragments are sifted upon white paper, and, without taking intensity into consideration, a judgment is formed at which degree of roasting the most beautiful color has been obtained.

B. Assay to determine the intensity.—The assay sample is fused in the above manner with different quantities of quartz (for instance, 1 to 10 times the quantity), and half the quantity of both of potash, to a homogeneous cobalt glass. Generally 2.5 grammes (38.59 grains) of the assay sample are taken when it has been mixed with once to twice the quantity of quartz, and 1.25 grammes (19.29 grains) if with more quartz, to prevent the crucibles from becoming too full. Too much quartz makes it difficult to fuse the mixture, and too much potassa gives smeary colors. A sample is taken from the smelted mass, cooled off, and dried. It is then pounded and sifted, or washed in spitz-glasses (Fig. 3, p. 28), and its color compared with that of a standard (muster), as to color and grain. This is done by spreading some of the standard color with a knife evenly upon a board, and placing a quantity, as large as a pea, of the assay sample upon it and pressing the latter into the former, when an experienced eye can tell in a well lighted room (not exposed to the direct rays of the sun) whether the assay sample corresponds with the standard in color-tone and grain, or not. If it should correspond in all respects, a confirmatory test is made by pressing some of the standard into the assay sample, when the same conditions must exist, and by examining the grain in both cases with a magnifying glass.

As moist smalt appears darker than dry, the standard and assay sample must stand for from 6 to 8 hours alongside of each other in a somewhat damp place, before the examination is made. The intensity of the color also increases with the coarseness of the grain, and an experienced eye and skilful hand are required to give the assay sample taken from the fused mass, the same grain as the standard with which it is to be compared. If the color of the assay sample is lighter than the standard with which it is compared, the assay must be repeated with a larger quantity of ore, and *vice versa*. If the color is not exactly the same, recourse is frequently had to mixing the product with lighter or darker varieties of smalt. An ore is the more valuable, the more quartz it requires for the production of a certain intensity of color.

VIII. ZINC.

45. ORES.

Smithsonite (*zinc carbonate*), $ZnCO_3$, with 52 Zn; *calamine* (*zinc silicate*), $Zn_2SiO_4 + 3H_2O$, with 53.7 Zn; *willemite*, Zn_2SiO_4, with 58.1 Zn; *zinc bloom*, $Zn_3CO_5 + 2H_2O$, with 57.1 Zn; *zinc blende*, ZnS, with 67.01 Zn; *zinkite*, ZnO, with 80.24 Zn; *franklinite*, (Zn, Fe) $(Fe_2Mn_2)O_4$, with 21 Zn.

46. DRY ASSAYS.

These are inaccurate, but give approximately the quality of the metal which may be expected from an ore (*distillation assay*), or the approximate percentage of zinc.

For many purposes they are sufficiently accurate (*indirect assay*).

A. Assay by distillation.—A mixture of 400 to 500 grammes (6172.94 to 7716.17 grains) of the comminuted assay sample with 80 to 100 per cent. of powdered charcoal, and, in case calamine is to be assayed, with 80 to 100 grammes (1234.58 to 1543.23 grains) of potash or calcined soda, is placed in a retort of refractory clay and heated in a furnace with a strong draught (Fig. 30, p. 56). The neck of the retort should project about 10 centimeters (3.93 inches). In it is luted a tube of glass or porcelain about 30 centimeters (11.81 inches) long, which is kept cool by moistened rags wrapped around it. The burning gases and the fumes escape from the end of the tube, while the zinc, mixed with oxide, which is distilled over, is mostly deposited in the neck of the retort and but little of it in the tube. After the "flaming" ceases, the tube should be frequently poked with an iron wire. The retort, after having been exposed to a white heat for several hours and the "flaming" having entirely ceased, is taken from the furnace and allowed to cool off. The metallic zinc is scraped from the neck of the retort, is placed in a crucible and fused with black flux and a covering of common salt. It is then poured out into an ingot mould and weighed. The retort is carefully broken into pieces, and all those having adhering to them either zinc or zinc oxide are collected together and placed in a porcelain dish, and the metal dissolved off by digestion with nitric acid. The solution is filtered and evaporated to dryness. The residue is heated to redness, the zinc calculated from the resulting zinc oxide, with 80.24 per cent. of zinc and added to the metallic zinc.

B. Indirect assay.—5 grammes (77.16 grains) of *zinc blende* are placed in a *covered* crucible (Fig. 39, p. 66) and heated under the muffle in order to expel the volatile substances. After it has been cooled off, it is weighed and the ignition repeated until a constant weight is obtained. The accurately weighed refractory residue is mixed with 3 grammes (46.30 grains) of iron filings free from rust, and 2.5 grammes (38.58 grains) of blast-furnace slag. The mixture is brought into a charcoal-lined iron crucible (Fig. 43, p. 67), covered with 2.5 grammes (38.58 grains) of blast-furnace slag, and the remaining space filled up with powdered charcoal. A loosely fitting cover is luted on. The charge is then heated at a white heat in the blast-furnace for $\frac{3}{4}$ to 1 hour, whereby iron sulphide is formed, while zinc volatilizes and the earthy substances fuse together with the iron slag. After the charge has become cool, the button consisting of brittle matt and slag is weighed, and its weight deducted from that of the refractory residue of the zinc blende *plus* 3 grammes (46.30 grains) iron filings, *plus* 5 grammes (77.16 grains) of iron slag. The difference will give the percentage of zinc. The fewer the metallic impurities in the blende, which would be separated by the iron and volatilized (such as antimony, lead, bismuth, etc.), the more accurate will this method be.

47. WET ASSAYS.[1]

Gravimetric and *volumetric* methods are used. Although the latter assay is somewhat less accurate than the former, it is nevertheless available in many cases for practical purposes.

A Gravimetric assays.

1. *Determination of zinc as zinc sulphide.*—1 gramme (15.43 grains) of the finely powdered assay sample,

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[1] B. u. h. Ztg. 1876, p. 148, 173 (Laur).

previously dried at 100° C. (212° F.), is placed in a long-necked flask and dissolved in nitric acid. Every trace of nitrous acid is removed by boiling, and the fluid is then strongly evaporated. 30 cubic centimeters (1.83 cubic inches) of nitric acid and about 200 cubic centimeters (12.2 cubic inches) of water are added, and the solution is then precipitated with sulphuretted hydrogen without previous filtration. The whole is now filtered off (metallic sulphides, quartz, etc.) and washed. A flask is now placed beneath the funnel, and its contents is treated with hot nitric acid not too concentrated. The filter is then perforated, the undissolved residue rinsed off into the flask, and the filter washed out. The fluid is strongly reduced by boiling, and then water and 30 cubic centimeters (1.83 cubic inches) of nitric acid are added. It is again precipitated with sulphuretted hydrogen, filtered, and the filtrate which carries some zinc is added to the principal zinc solution. The entire filtrate is then boiled nearly to dryness in the long-necked flask in order to remove the sulphuretted hydrogen, some potassium chlorate being added for the higher oxidation of any ferrous oxide. The mass is then supersaturated with pure ammonia, the iron precipitate filtered off, washed and dissolved in hot, medium strong nitric acid. It is now again precipitated with ammonia to extract any residue of zinc, and filtered through the same filter, these manipulations being repeated once or twice more. The entire filtrate is now acidulated with acetic acid, diluted to the volume of at least 2 liters (3.52 pints), sulphuretted hydrogen is introduced (in the absence of nickel and cobalt), and the liquid is then allowed to stand for 24 hours. The clear liquid is then poured off upon a filter, and finally the zinc sulphide. The flask is rinsed out with sulphuretted hydrogen water, the precipitate is also washed with it with the addition of some ammonium acetate. The filtrate from the zinc sulphide is supersaturated with ammonia and allowed to stand for at least 24 hours in a covered glass in order to see whether any zinc sulphide is still deposited. The filter is dried, and the zinc sulphide adhering to it detached by rubbing, the filter being entirely closed during the operation. The zinc sulphide, together with the ash of the filter and some distilled sulphur, is heated in one of *Rose's* crucibles (Fig. 52, p. 122) until it commences to frit, and then in a current of dry hydrogen until two weighings correspond ($ZnS = 67.01$ Zn). The determination of zinc as zinc sulphide is *very* accurate.

2. *Determination of zinc as zinc oxide.*—1 gramme (15.43 grains) of ore is dissolved in *aqua regia*, and ammonia in excess and ammonium carbonate are added, whereby zinc (and copper) passes into solution. The resulting precipitate (iron, lead, etc.) is again dissolved and precipitated, and ammonia added to extract any remaining traces of zinc. The zinc (and copper) is then precipitated from the filtrate with sodium sulphide, and filtered. The zinc sulphide is separated from the copper sulphide upon the filter by treating with diluted hydrochloric acid, and the copper sulphide remaining behind is washed. The zinc is precipitated in the boiling filtrate by means of sodium carbonate, washed, dried, ignited, and weighed as zinc oxide containing 80.24 per cent. of zinc.

The zinc may also be precipitated from the neutralized filtrate from the copper sulphide by means of sodium sulphide, and determined as zinc sulphide (p. 204). This assay is less accurate than the foregoing one.

3. *Galvanic assay*, according to Beilstein and Jawein.[1]

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[1] Liebig's Jahresber. 1865, p. 686 (Luckow); Fresenius' Ztschr. xv. 303 (Wrightson); xvi. 469 (Parodi und Mascazzini). B. u. h. Ztg. 1878, p. 26 (Riche). Ber. d deutsch. chem. Ges. 1879, No. 5, p. 446 (Beilstein und Jawein).

—0.5 to 1 gramme (7.71 to 15.43 grains) of ore is dissolved in nitric or sulphuric acid, and caustic soda added until a precipitate is formed. Solution of potassium cyanide is gradually added until the solution becomes clear, and then the platinum electrodes (p. 117) are immersed in the solution. The current of 4 *Bunsen* elements (the cylinder of zinc 15.5 centimeters (6.1 inches) high, the carbon dipping into nitric acid, with which 0.1 gramme (1.54 grains) of zinc will be precipitated per hour) is then passed through the liquid. The beaker-glass containing the solution should be placed in a dish of cold water, to prevent it, in case but a small quantity is being operated on, from becoming strongly heated by the action of the electric current. When precipitation is supposed to be complete, the electrodes are lifted out of the fluid, the zinc is first washed off with water, next with alcohol, and finally with ether, and then dried in the desiccator. After being weighed, the zinc is dissolved from the platinum with hydrochloric or nitric acid, and the electrodes are again placed in the fluid in order to test it for any residual zinc. Black stains, which may be perceived upon the electrodes, after the zinc has been removed, originate from finely divided platinum.

When *copper* is present (as for instance with brass), the sample is dissolved in nitric acid and evaporated to dryness. The residue is taken up with water, and the copper precipitated by electrolysis from the solution previously acidulated with nitric acid, when *lead* will be deposited on the platinum spiral as peroxide. The zinc is then precipitated as above described.

B. Volumetric assays.—Of the volumetric assays which have been recommended—

1. *Schaffner's assay with sodium sulphide*[1] is used

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[1] B. u. h. Ztg. 1856, p. 231, 306; 1857, p. 60 (Schaffner); 1876, p. 148, 174 (Laur); p. 225 (Thum); p 304 (Tobler). Journ. f. prakt. Chem.

more than any other. This is based upon the precipitation of zinc from ammoniacal solution by means of sodium sulphide. The termination of precipitation is indicated by the blackening of ferric hydrate as below described. This assay, if certain precautionary measures are adopted, allows of a determination of the zinc to within 0.5 per cent. The presence of metals soluble in ammonia (*copper* and *manganese; nickel* and *cobalt* occur but seldom) requires modifications of the method.

0.5 gramme (7.71 grains) of *oxidized ores* (smithsonite, calamine), with over 35 per cent. of zinc, and more, if the ore is poorer, are dissolved in heated hydrochloric acid, with an addition of a few drops of nitric acid, to oxidize the iron; the solution is then supersaturated with ammonia: or, raw, or roasted zinc blende is dissolved in *aqua regia*, evaporated to dryness, and the residue dissolved in 5 cubic centimeters (0.3 cubic inch) of hydrochloric acid and some water. *Copper* (also lead, antimony, etc.) being frequently present, the solution is precipitated with sulphuretted hydrogen, filtered, and the gas driven off by boiling. 10 cubic centimeters (0.61 cubic inch) of *aqua regia* are added (or some chlorine water, or a few drops of bromine may be added to the acid solution, or potassium permanganate to faint reddish coloration to the ammoniacal solution, and allowing it to stand for one hour) for the higher oxidation of the *iron* and *manganese* (if iron alone is present, an addition of nitric acid or potassium chlorate suffices), which, when ammonia in excess is added, are precipitated as hydrated

lxxxviii. 486 (Küntzel). Fresenius' Ztschr. 1870, p. 465 (Deus); 1871, p. 209 (Schott). Mohr, Titrirmethode, 1874, p. 466 (F. Mohr). Dingler, cxlviii. 115 (C. Mohr). Preuss. Ztschr. Bd. 25 (Hampe). Berggeist, 1874, No. 3 (Altenberger Pr.). Berichte der deutsch. chem. Ges. 1879, No. 3, p. 270 (Aarland).

oxides, while the zinc remains in solution. The hydrated oxides are again dissolved in hydrochloric acid and precipitated with ammonia in excess, in order to extract any residue of zinc. Both filtrates are then united and diluted (to 500 cubic centimeters (30.51 cubic inches) if 5 grammes (77.16 grains), and to 175 to 225 cubic centimeters (10.67 to 13.72 cubic inches) if 0.5 gramme (7.71 grains) of ore have been used). 50 cubic centimeters (3.05 cubic inches) of the fluid are then placed in a beaker-glass, 1 to 2 drops of a solution of ferric chloride of the concentration given below are dropped into 1 cubic centimeter (0.061 cubic inch) of ammonia contained in a porcelain saucer. The precipitated hydrated ferric oxide is carefully rinsed into the beaker-glass, where it settles on the bottom. Titrated solution of sodium sulphide (1 cubic centimeter (0.061 cubic inch) = 0.008 to 0.009 gramme (0.12 to 0.14 grain) of zinc) is then added, the contents of the beaker-glass being given a spiral motion in the mean while, so that the flakes remain on the bottom. The addition of the sodium sulphide is continued until flakes of ferric oxide become discolored, and finally assume a brown color, which indicates that all the zinc has been precipitated.[1]

The following have also been recommended as *indicators* for recognizing the final reaction; though none of them have taken the place of the hydrated ferric oxide. Porcelain saturated with ferric chloride (*Barreswill*), or paper (*Streng*) which is weighted with platinum wire and laid upon the bottom of the beaker-glass; drop samples (Tupfproben) with nickel chloride (*Küntzel*), cobaltous chloride (*Deus*), alkaline solution of lead tartrate (*F. Mohr*); blotting-paper saturated with sugar of lead, and then treated with ammonium carbonate (*Fresenius*); nitro-prussiate of sodium (*C. Mohr*); sized paper coated with white lead, so-called "polka" paper (*Schott*), over which filtered drops of the fluid are allowed to run.

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[1] It is advisable to have a stand with three burettes respectively for solution of zinc, sodium sulphide, and ferric chloride.

The following points must be observed in order to make the assay successful.

a. The quantity of the hydrated ferric oxide, which is added, must not vary too much, and must possess a uniform coherence. This may be produced by dissolving 3 grammes (46.30 grains) of piano wire in *aqua regia*, and diluting this to a bulk of 100 cubic centimeters (6.1 cubic inches). The same number of drops of this solution are allowed to fall each time, for instance from a burette, into 1 cubic centimeter (0.061 cubic inch) of concentrated ammonia (p. 209). The ring-like clot of hydrated ferric oxide which will be formed in about one minute may then be rinsed into the fluid which is to be titrated.

b. The same shade of coloration of the hydrated ferric oxide used in the operation should always be taken as closely as possible to indicate the end of the reaction, as the quantities of sodium sulphide consumed in producing various shades vary considerably.

c. The quantity of fluid, into which the added excess of sodium sulphide is divided in titrating, exerts a material influence in respect to its action upon the hydrated ferric oxide, as, when the quantity of fluid becomes smaller, a smaller excess of sodium sulphide suffices for blackening the hydrated ferric oxide.

In consideration of this circumstance, the volume of liquid is measured, according to *Tobler*, in the smelting works of the *Vieille Montagne*, at the termination of the titration, and for each 100 cubic centimeters (6.1 cubic inches) of it, the volume of sodium sulphide consumed is decreased 0.7 and 0.5 cubic centimeter (0.042 and 0.03 cubic inch), its standard being 0.008 to 0.009 gramme (0.12 to 0.14 grain) of zinc to 1 cubic centimeter (0.061 cubic inch). According to *Thum*, this correction can be avoided, by always bringing all the liquids before titration to an equal volume, and by using so much zinc for standardizing as corresponds to the average percentage, and the quantity of zinc ore used. This zinc is dissolved and the solution diluted to a volume equal to that of the solution of the ore, and the titer of this is taken. Under these conditions there can be no material difference in the quantities of sodium sulphide consumed in fixing the standard of the solution and of those consumed in the analyses, and therefore the quantities of liquid must be nearly equal after the titration, and in consequence of this no errors can occcur on account of differences of volumes.

d. It does not make any difference, as far as the accuracy of the assay is concerned, whether the hydrated ferric oxide is introduced at the commencement, or towards the end of the titration, if the same order is always observed. The heating of the liquid exerts also but little influence.

e. Admixtures having a disturbing effect must be removed. *Copper*, *silver*, *cadmium*, *cobalt*, *nickel*, *chromium*, *manganese*, *arsenic*, and *antimony* are soluble in ammonia, and also *lead* in small quantities, which last, after the precipitation with ammonia, may be present either as carbonate, sulphate, and basic chloride, or as oxy-salt. Of these, the last two are the more soluble in ammonia. *Copper*, *lead*, *manganese*, and *iron* occur most frequently.

Copper, together with cadmium, silver, arsenic, and antimony, is removed by sulphuretted hydrogen. If a small quantity only is present, it can be determined by *Heine's* colorimetric assay, and titrated with sodium sulphide, notwithstanding the blue coloring of the ammoniacal zinc solution, and the total consumption of sodium sulphide, reduced by the volume corresponding to the percentage of copper found. *Manganese* is the least injurious of all, and can be easily removed as above described, p. 208. It becomes sulphurized later than the hydrated ferric oxide, and the percentage of zinc can be accurately determined by taking the commencement of the blackening of the hydrated ferric oxide as indicator of the final reaction, and not continuing until it has turned entirely black. But it is best to first remove the manganese by precipitation in case a considerable percentage of it is prese This fact may be recognized by a concentrated acid solution, notab losing its originally dark color, upon dilution. *Lead* is removed b sulphuretted hydrogen with the copper, or by evaporating the substance to dryness with sulphuric acid, after the preliminary treatmen with acids, then taking up with diluted sulphuric acid, and removing the lead sulphate by filtration, etc. When more than 5 per cent. of iron is present, the ammoniacal precipitate must always be redissolved at least once. Organic substances, which are sometimes found in foreign zinc ores, are destroyed by heating to redness with free access of air, as otherwise they might easily reduce the ferric oxide to ferrous oxide, which is soluble to some extent in ammonia, and decomposes sodium sulphide.

f. The *zinc* used for fixing the standard solution must be sufficiently *pure.*

Good commercial zinc is purified by smelting 50 grammes (771.61 grains) in a porcelain crucible over a lamp; keeping it in this state for a quarter of an hour, poling it with a wooden stick. The layer of oxide is then taken off, and, after the metal has stood for a few minutes, one-half of it is poured into another crucible, where the same operation is repeated. Half of the metal is again poured off, these manipulations being repeated several times. The zinc is then dropped upon a cold zinc plate (the surface of which must be free from oxide) so that each drop forms a small thin disk that may be readily broken to fragments. It should be kept under a bell-glass with calcium chloride. The *American Passaic* zinc is very pure.

g. There should be a *uniform light* in the room during the titration, so as to enable the operator to observe correctly the coloring of the iron. This is best arranged by covering the windows with tracing linen or tissue paper (Altenberg).

2. *Assay with potassium ferrocyanide.*[1]—The zinc is precipitated from an acid solution by potassium ferrocyanide, uranic salt being used as an indicator. When

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[1] Dingler, ccxv. 260 (Galletti); Fresenius' Ztschr. 1875, pp. 189, 343, (Lyte and Galletti); 1874, 379 (Fahlberg); Dingler, ccx. 229 (Renard); ccx. 395 (Reindl).

all the zinc is precipitated, the uranium salt produces a brownish stain, when a test is made by taking a drop upon a white plate. 5 grammes (77.16 grains) of ore are dissolved in aqua regia, and evaporated. Hydrochloric acid in excess is added to the residue, the copper, etc., are precipitated with sulphuretted hydrogen and filtered. The filtrate is boiled, the ferrous oxide is oxidized by potassium chlorate, and ammonia is added. The ferric oxide and alumina are then filtered, and again dissolved and precipitated. The filtrate is neutralized with hydrochloric acid and an additional 10 to 15 cubic centimeters (0.61 to 0.91 cubic inch) of hydrochloric acid of 1.12 specific gravity are added. The solution is then titrated with the solution of potassium ferrocyanide (1 cubic centimeter (0.061 cubic inch) = 0.01 gramme (0.15 grain) of zinc) until the appearance of the first brownish stain by the drop test with solution of uranic salt.

3. *Schober's volumetric assay.*[1]—The zinc is precipitated with alkaline sulphide solution. The excess of sulphide used is decomposed with silver solution, and finally the quantity of the solution of silver, which has been added in excess and remained undecomposed, is determined by ammonium sulpho-cyanide according to Volhard's method (p. 156).

IX. CADMIUM.

48. ORES.

It occurs more seldom as an ore (*greenockite*, CdS, with 77.6 Cd) than as a constituent of calamine and zinc blende.

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[1] Oestr. Ztschr. 1879, 5.

49. GALVANIC ASSAY.[1]

Cadmium sulphide is precipitated from an acid solution with sulphuretted hydrogen. This (and also cadmium oxide) is dissolved in nitric acid, the free acid is neutralized with caustic potassa, with an addition of potassium cyanide solution, until the precipitate is dissolved. It is then diluted with a sufficient quantity of water, so that about 0.2 gramme (3 grains) of cadmium are contained in 75 cubic centimeters (4.57 cubic inches) of the liquid. The cadmium is then precipitated upon the platinum cone (p. 117) with 3 Bunsen elements, the glass containing the liquid being placed in a dish filled with cold water. The rate of precipitation should be from 80 to 90 milligrammes (1.23 to 1.38 grains) of metal per hour. The light gray cadmium is rinsed off with water, then with alcohol, and dried by placing it in a heated platinum dish (p. 118).

X. TIN.

50. ORES.

Tinstone (*cassiterite*), SnO_2, with 78.7 per cent. tin.

51. DETERMINATION OF TINSTONE BY WASHING.

This method is used for testing borings from mines, in order to ascertain whether poor tin ores are worth working (Saxony); or in concentrating works, to determine the quantity of material worth smelting which may be obtained from an ore-heap (Cornwall). The specific gravity of tinstone = 6.8 to 7.0.

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[1] Berichte der deutsch. chem. Ges. 1879, No. vii. p. 759.

A. Saxon assay of tin.—A sample of dust, taken by volume, is washed in the vanning trough (Fig. 4, p. 29).

B. Determination of tin by washing in Cornwall.[1]—50 kilogrammes (110 pounds) of samples are taken from different parts of the heap. The mass is comminuted and thoroughly mixed. From this, another sample is taken, sifted, and dried, and 55 to 56 grammes (848.77 to 864.21 grains) of it are weighed off. This is placed upon an iron shovel, and washed, by imparting to it, first a rotary motion, and then a decided upward and downward movement. By these operations, the products free from tin will be washed away, while those yielding tin will, according to their specific gravity, be collected on different parts of the shovel. They are then removed, and, if necessary, roasted, and again washed. This manipulation requires considerable skill.

52. FIRE ASSAYS.

The object of these is to reduce the tin oxide (stannic acid) and slag off the admixtures of earths by solvent fluxes. The accuracy of the result is impaired, or the assay is made difficult, on account of the tin oxide being easily slagged off by acids and bases; by the difficulty of uniting the reduced particles of tin to a *single* button; and by the presence of many foreign metallic combinations and earths which promote the slagging off or the contamination of the tin.

The losses by the *German* method are less than by the *English* or *Cornish* method. The assay with potassium cyanide gives the highest yield. The tin buttons obtained by the fire assay must be tested in the wet way for the presence of copper, iron, etc., by treating them with nitric acid of 1.3 specific gravity, adding water, digesting, filtering, drying, igniting, and weighing the tin oxide.

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[1] B. u. h. Ztg. 1859, p. 358. Muspratt's Chemie, vii. 1375.

A. German assay.—5 grammes (77.16 grains) of clean ore are intimately rubbed together with 0.75 to 1 gramme (11.57 to 15.43 grains) of powdered charcoal. The mixture is poured into a suitable crucible (Fig. 42, p. 67), and covered with 12.5 to 15 grammes (192.90 to 231.48 grains) of carbonaceous black flux or potash with 50 per cent. of flour, 1 to 1.25 grammes (15.43 to 19.29 grains) of borax glass, and finally with a cover of common salt and a small piece of coal. The charge is exposed for three-quarters to one hour to a very strong red heat in the reverberatory (p. 59) or muffle furnace (p. 49), or for one-half to three-quarters of an hour in the blast furnace (p. 60). The crucible is then taken out and allowed to become entirely cold, as tin has a low fusing point. It is then freed from slag, and the result must be a single, ductile button of a tin-white color, which does not follow the magnet under water. In case the tin is distributed in the slag, this must be washed off and the metal collected.

Other charges: 25 grammes (385.80 grains) of ore, 5 grammes (77.16 grains) of argol, 20 grammes (308.64 grains) of soda, and 3 grammes (46.30 grains) of lime, are intimately mixed together, and covered with a layer of soda and 10 grammes (154.32 grains) of borax. The charge is smelted at a strong red heat and kept in fusion for twenty minutes. Or for siliceous ores: 10 grammes (154.32 grains) of ore, and from 10 to 20 grammes (154.32 to 308.64 grains) of fluor-spar or cryolite are placed in a charcoal-lined crucible and covered with charcoal. A lid is luted on, and the charge is then very strongly heated for one hour. This assay gives a good yield.

Modifications become necessary—

1. When the ore contains many earthy admixtures. The ore, before it is reduced, must be washed in a vanning trough (Fig. 4, p. 29), in spitz-glasses (Fig. 3, p. 28), or in a beaker-glass (as silicic acid especially promotes slagging off of tin). This manipulation is effectual on account of the high specific gravity of tin, but metallic admixtures cannot (or can only partly) be removed by it.

Specific gravities: tinstone, 6.8 to 7; native bismuth, 9.6 to 9.8; tungsten, 7.2 to 7.5; arsenical pyrites, 6 to 6.4; copper glance, 5.5 to 5.8; iron pyrites, 4.9 to 5.1; copper pyrites, 4.1 to 4.3; molybdenite, 4.5 to 4.6; magnetic iron ore, 4.8 to 5.2; specular iron ore, 6 to 6.5; red hematite, 4.5 to 4.6; zinc blende, 3.9 to 4.2; quartz, 2.65 to 2.80; chlorite, 2.65 to 2.85; slate, 2.5.

2. When the ore contains *foreign metallic sulphides, arsenides*, and *antimonides*.

a. The unroasted ore is either digested with *aqua regia* for half an hour, and then washed by decantation, the tungstic acid, from tungsten ores, if any be present, removed by digesting with caustic ammonia for half an hour (the flask being frequently shaken), then washed by decantation and dried (*Levol*[1]), and then reduced:

b. Or, the dead-roasted ore is treated with hydrochloric acid as long as the acid, after the ore has been repeatedly decanted and washed, appears yellow, when a fresh addition is made at a boiling temperature; the ore is then washed by decantation, dried, and subjected to reducing and solvent fusion as above described (p. 215).

3. *On account of the ease with which tin oxide is slagged off.*—For this reason—

a. The ore is intimately rubbed together with powdered charcoal (p. 216), or carbonaceous black-flux, but too large a percentage of carbon will render the charge more refractory.

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[1] Polyt. Ctrbl. 1857, p. 406.

b. The tin oxide is reduced, before the reducing and solvent fusion, by mixing the ore with $\frac{1}{5}$ part of powdered wood charcoal and igniting it in the crucible. It is then charged as above.

4. When *separate grains of tin are found.*—These must be collected with copper (bronze being formed), by mixing 5 grammes (77.16 grains) of ore with 5 grammes (77.16 grains) of pure copper oxide (with 79.14 Cu). The mixture is placed in a suitable crucible (Fig. 42, p. 67) and 15 grammes (231.48 grains) of black flux and 1.25 grammes (19.29 grains) of borax-glass are added, a cover of common salt and a fragment of coal. The charge is gradually heated to a high temperature, and, after the "flaming" has ceased, is exposed for three-fourths to one hour to a white heat in the muffle or wind furnace, or for one-half to three-fourths of an hour in the blast furnace. It is then taken out, and, when it has become cold, the brittle bronze button is freed from slag and weighed. The weight of the copper contained in the copper oxide, which was added, is deducted. If the copper oxide is not entirely pure, 5 grammes (77.16 grains) of it are fused with the same additions as given above and the weight of the resulting copper button is deducted from that of the bronze button.

5. When tin oxide is combined with silicate (as, for instance, in tin-ore slags), 5 to 25 grammes (77.16 to 385.80 grains) of slag are rubbed as fine as possible, the metallic tin is sifted out and the fine substance is gradually introduced in 12 to 15 times the quantity of potassium bisulphate which has been previously fused in an iron or porcelain crucible under the muffle. The mixture is then fused until no more gas bubbles are formed. The fused mass is then extracted with boiling water, next washed with hot water, and the residue reduced as above.

Or, 25 grammes (385.80 grains) of slag are mixed with 10 grammes (154.32 grains) of ferric oxide, 6 grammes (92.59 grains) of fluor-spar, and 100 grammes (1543.23 grains) of charcoal powder. The mixture is placed in a covered crucible and gradually heated to a strong red heat. This is kept up for half an hour, and finally kept at a white heat for half an hour longer.

B. Cornish assay of tin.—50 to 100 grammes (771.61 to 1543.23 grains) of rich tinstone are mixed with one-fourth the quantity of anthracite and some fluor-spar. A large wind furnace, such as is used for assaying iron (for instance, 254 millimeters (10 inches) wide, 178 millimeters (7 inches) long, and 380 millimeters (14.93 inches) deep), is filled about two-thirds full with coke, and brought to a strong red heat. A few pieces of fresh coke are then added, and in these a graphite crucible is placed and made red hot. It is then taken out, the charge poured into it by means of an open mixing scoop, and the crucible covered. The charge is then fused for 20 minutes, when the white-hot crucible is taken out, and the contents is poured into an iron ingot mould. The ingot is freed from slag. The slag is pounded fine and sifted through a sieve of tin plate having meshes about as large as a pin-head. The tin remaining in the sieve is added to the ingot of tin, while the fine stuff that has passed through the sieve is washed and floated in a vanning trough (Fig. 4, p. 29). The metallic residue from the washing is placed in a dish and dried. The three lots of tin are then weighed together. The ingot of tin is now refined by smelting it in an iron spoon. The film which is formed during this operation is removed until the liquid metal has a bright non-iridescent surface. It is then poured into a gutter in a marble plate, and the quantity of the tin judged by the surface and ductility of the resulting rod of metal. When lead and copper are present, the surface will exhibit a play of colors and will be crystalline, especially towards the centre. This assay yields about 10 per cent. less than the true percentage.

The Cornish assay is less accurate than the German, but an experienced assayer obtains results which compare well with those obtained on a large scale, and it allows him to form a judgment of the quality of tin which an ore may be expected to yield, and to fix the price to be paid for it accordingly.[1]

C. Levol's assay with potassium cyanide.[2]—A sufficient quantity of powdered potassium cyanide is rammed into a capacious porcelain or fire-clay crucible to form a layer of from 12 to 15 millimeters (0.47 to 0.59 inch) thick, 5 grammes (77.16 grains) of the powdered ore, intimately mixed with 5 times the quantity of potassium cyanide, are added to that in the crucible, and the whole covered with a thin layer of the cyanide. The charge is then heated in a moderate fire until it fuses, and is kept in constant fusion for 10 minutes. The crucible is then taken out, and gently tapped to facilitate the formation of a single button, and allowed to cool. The button is then freed from adhering slag by water. In case copper or lead is present, the ore must be freed from them before the reduction, by treating it with acid. This is the most accurate method of assaying tin (to within one-half per cent.), and can be executed in a very short time. In case the ore is siliceous, a mixture of 10 grammes (154.32 grains) of ore, 3 to 8 grammes (46.30 to 123.5 grains) of ferric oxide, and 40 grammes (617.53 grains) of potassium cyanide is placed in a crucible (Fig. 49, p. 117) lined with charcoal. The mixture is first covered with potassium cyanide and then with powdered charcoal. The cover is luted on and the charge heated at a high temperature for one-half to one hour.

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[1] B. u. h. Ztg. 1862, p. 261.

[2] Journ. für prakt. Chemie, xcv. 503.

53. WET ASSAYS.

A. Gravimetric assays.

1. 1 gramme (15.43 grains) of tinstone is digested with diluted *aqua regia*; the residue is washed by decantation and dried. The dry mass is then fused with 3 parts sulphur and 3 parts sodium carbonate. The soluble double sulpho-salt of sodium and tin is lixiviated with water, and the tin sulphide precipitated with hydrochloric acid. Sulphuretted hydrogen is then introduced into the liquid the resulting precipitate is filtered, dried, roasted, and finally weighed as stannic acid, containing 78 per cent. tin. By another method the ore is digested in *aqua regia* for half an hour, then washed by decantation and dried. It is then introduced into a silver crucible, standing in a clay crucible, with 4 times the quantity of caustic potassa (this is dissolved in water, the very finely powdered tinstone is stirred into it, and brought to dryness). It is then fused at a low red heat for half an hour. The mass, when cold, is treated with diluted hydrochloric acid and evaporated to dryness. The dry mass is then taken up in some hydrochloric acid, gently heated, filtered, and precipitated with sulphuretted hydrogen. The tin sulphide is washed, dried, and roasted, some ammonium carbonate being added towards the end of the operation. The tin oxide is then weighed.

2. The ore is digested with *aqua regia*, the residue with some charcoal is placed in a porcelain crucible and heated to redness. The reduced tin is dissolved in hydrochloric acid, and precipitated from the solution with zinc,

which, in the form of a flat button fastened on the end of a copper wire, is suspended in the fluid. According to the proportion of free acid present, the tin will appear in brilliant needles, in scales, mossy or spongy; the latter condition indicates the termination of precipitation. The zinc button is now taken from the liquor, freed from the tin, and this is pressed together in an agate mortar. It is then dried and fused to a button with some stearine (Moissenet[1]). Or, the ore is digested with *aqua regia*, decomposed with potassium hydrate, and a solution of stannic chloride in hydrochloric acid is formed as above. The tin is precipitated by a rod of zinc. It is then washed and dried, treated with strong nitric acid, and evaporated to dryness. When cold, it is moistened with diluted nitric acid and filtered. The tin oxide is then dried, ignited, and weighed. Lead and copper are removed by the *aqua regia* at the commencement of the operation, or when the precipitated tin is dissolved in nitric acid.

B. Volumetric assays.

1. *Determination of tin by means of iodine.*—A few drops of potassium iodide of any desired concentration are added to the acid solution of stannous chloride, and then a few drops of diluted starch paste. A solution of potassium bichromate of 0.02 or 0.01 gramme (0.3 or 0.15 grain) of the salt in 1 cubic centimeter (0.61 cubic inch) is now added drop by drop under constant stirring, until the separated iodine does not again disappear, and the starch assumes a blue color when all the stannous chloride has been converted into stannic chloride ($3SnO + Cr_2O_6 = 3SnO_2 + Cr_2O_3$). The quantity of chromate decomposed by 100 parts of pure tin dissolved in

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[1] B. u. h. Ztg. 1861, p. 170.

hydrochloric acid is empirically determined (100 tin = 83.2 chromate).

1 to 2 grammes (15.43 to 30.87 grains) of tinstone are placed with four times the quantity of potassium cyanide in a porcelain dish, and heated for fifteen to twenty minutes. The mass is then poured upon an iron plate and treated with water. The metallic residue (tin and iron) is dissolved in hydrochloric acid, the tin precipitated with zinc, again dissolved in hydrochloric acid, and titrated with potassium bichromate in the presence of potassium iodide and starch. (*Hart.*)[1]

According to *Lenssen*,[2] more accurate results may be obtained by dissolving stannous salts (stannous chloride) with an addition of tartaric acid, or potassium-sodium tartrate, in sodium bicarbonate. Some starch paste is added to the clear solution, and it is then titrated with solution of iodine until the blue color appears ($SnO + 2I + Na_2O = SnO_2 + 2NaI$). The iodine solution is standarized by dissolving 12.7 grammes (196 grains) of pure iodine, and 20 to 30 grammes (308.64 to 462.97 grains) of potassium iodide in 1000 cubic centimeters (61.02 cubic inches) of distilled water. A quantity of pure tin, accurately weighed, is dissolved in hydrochloric acid, tartaric acid is added, and the solution supersaturated with sodium bicarbonate. Solution of starch is added, and the iodine solution is gradually added from the burette until the liquid becomes blue. Two atoms of iodine (254) correspond to one atom of tin (118). This [illegible] may be especially recommended for the detection of [illegible] quantities of tin.

2. *Determination of tin by means of potassium permanganate.*—5 to 10 cubic centimeters (0.3 to 0.61 [illegible] inch) of solution of stannous chloride are treated [illegible]

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[1] Dingler, ccx. 394.

[2] Journ. f. prakt. Chem. lxxviii. 200. Mohr, Titri[illegible] [illegible] 311.

boiling solution of ferric chloride containing free hydrochloric acid ($SnCl_2 + Fe_2Cl_6 = SnCl_4 + 2FeCl_2$). The ferrous chloride which is formed is titrated, after dilution with water, with standard solution of potassium permanganate, until the liquid becomes reddish (p. 127). The value of the standard solution is determined by placing 0.2 gramme (3.08 grains) of freshly precipitated tin in a platinum crucible, and dissolving it in hydrochloric acid, in a current of carbonic acid. Ferric chloride in excess is added, and solution of potassium permanganate is then added, until the last drop colors the fluid perceptibly. 2 equivalents of iron = 1 equivalent of tin. A correction becomes necessary, as experience has shown that more potassium permanganate is consumed in titrating ferrous chloride than stannous chloride.

XI. BISMUTH.

54. ORES.

Native bismuth, *bismuth glance*, Bi_2S_3, with 81.25 Bi; *cupriferous bismuth*, $CuBiS_2$, with 62 Bi and 18.9 Cu; *tetradymite*, Bi_2Te_3, with 51.94 Bi; *bismuth ochre*, Bi_2O_3, with 89.65 Bi, and others.

55. FIRE ASSAYS.

These are inaccurate, as bismuth votalizes, and, in case the ore is impure, foreign metals collect in the brittle button.

1. *Ores and compounds free from sulphur* (native bismuth, tetradymite, bismuthic cupel ash, etc.). 5 grammes (77.16 grains) of ore with two and a half to three times the quantity of black flux, or potash and flour, and 2.5 to 5

grammes (38.59 to 77.16 grains) of borax-glass, are placed in a suitable crucible (Fig. 42, p. 67) and covered with a layer of common salt. It is then placed in the muffle, and, after the "flaming" has ceased, fused for twenty-five to thirty minutes at not too high a temperature. Or, 10 to 20 grammes (154.32 to 308.64 grains) of the substance are heated with two and a half to three times the quantity of borax-glass, an equal weight of soda, and 5 to 10 grammes (77.16 to 154.32 grains) of potassium cyanide, with a covering of common salt. Lead, tin, and copper pass partly into the bismuth, and must be removed by the wet method.

2. *Sulphurized bismuth ores.*—Five grammes (77.16 grains) of ore are placed in a crucible and covered with 1.25 to 1.5 grammes (19.29 to 23.15 grains) of thick iron wire and 2.5 to 10 grammes (38.58 to 154.32 grains) of fine shreds of silver; upon this is placed two and a half to three times the quantity of black flux or potassium carbonate, and flour, on this 1½ to 2 grammes (23.15 to 30.86 grains) of borax, and a covering of salt. The charge is fused as in the lead assay, when the sufficiently ductile alloy of silver with bismuth can be separated from the iron. The percentage of bismuth is found by deducting the added silver. *Arsenic* must be removed by a previous ignition of the ore, with exclusion of air; but *antimony*, with an admittance of air. *Lead* passes into the bismuth, and *copper*, if not too much of it is present, is slagged off.

Joachimsthal: 5 grammes (77.16 grains) of ore are fused with 2 grammes (30.87 grains) of sodium carbonate and 1.25 grammes (19.29 grains) of iron turnings with a covering of common salt. The resulting plumbiferous button is dissolved in nitric acid, the lead is separated as lead chloride by *Patera's* method, which will be given later on, or the bismuth separated, as metal, from a weak acid solution by means of a strip of *lead*. *Tamm's process:* Ore free from copper is fused with a flux consisting of 2 parts potassium or sodium carbonate and 1 part common salt with an addition of some potassium cyanide. *Cupriferous ores:* 3 parts of ore with 5 parts potassium or sodium carbonate, 2 parts common salt, 1 part powdered wood-charcoal, and 2 parts flowers of sulphur. The bismuth is separated (with about 8 per cent. loss), containing a little copper, most of the latter passing into the slag as sulphide. The presence of iron induces more copper to unite with bismuth; antimony and arsenic and lead (partly) pass into the slag. *Rose* fuses the ore with 5 times the quantity of potassium cyanide, in a porcelain crucible, washes the resulting metal grains quickly with water, then with dilute alcohol, and weighs. In fusing, no black pulverulent residue of bismuth sulphide must remain.

56. WET ASSAYS.

While the *volumetric assays*[1] which have been recommended are of no practical importance, the gravimetric methods are mostly complicated, the available docimastic tests being, as a general rule, limited to the separation of bismuth from lead.

A. Assay of ore.—2 to 3 grammes (30.87 to 46.30 grains) of ore are dissolved in nitric acid, and evaporated to dryness. Some sulphuric acid is then added, the mass stirred, and again evaporated to dryness. The residue is now dissolved in water, and filtered. The filtrate is precipitated with ammonium carbonate in excess, filtered off, washed, dried, ignited, and then weighed as oxide, containing 89.65 per cent. bismuth.

B. Separation of bismuth from lead.

1. *According to Patera.*—The plumbiferous bismuth is dissolved in nitric acid. The solution is considerably

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[1] Fleischer, Titrirmethode, 1876, p. 87. Muir, in Ber. d. deutsch. chem. Gesel. 1877, p. 2051. Buisson, in Fresenius' Ztschr. 1874, p. 61. Pearson, in Mitchell's Practical Assaying, 1868, p. 643.

diluted with water, upon which the liquid must not become turbid. The bismuth is then precipitated from the weak acid solution with a bright strip of lead. The pulverulent black bismuth is removed, and washed with water and alcohol. It is then dried at a temperature not over 120° C. (248° F.), and weighed. Or, hydrochloric acid in excess is added to the diluted nitric acid solution and then some strong alcohol; the silver chloride and lead chloride are filtered off, and the bismuth is precipitated from the filtrate with ammonium carbonate. The carbonate is washed, dried, and ignited, and the bismuth determined as oxide (Bi_2O_3 with 89.65 Bi).

Determination of the percentage of *lead* and *silver:* The combined metallic chlorides are weighed upon a weighed filter and then cupelled. The silver is calculated to silver chloride, the yield deducted from the weight of the combined chlorides, and the lead calculated from the lead chloride found by difference. *Copper* is determined by evaporating the ammoniacal filtrate to dryness with sulphuric acid. The dry mass is taken up in water, and the copper precipitated with iron or zinc (p. 111).

2. *According to Ullgreen.*—The solution of bismuth in nitric acid is precipitated with ammonium carbonate. The lead and bismuth carbonates are dissolved in acetic acid, and the bismuth is precipitated in a well-closed vessel with a bright strip of lead. It is then filtered, washed, and dissolved in nitric acid. The mass is then evaporated to dryness and heated, when bismuth oxide remains behind.

Tin oxide (also antimonious acid) remains behind in nitric acid in dissolving the alloy. The residue is then washed with alcohol, dried and weighed. *Lead* and *bismuth* are precipitated from the filtrate with ammonium carbonate (see above), and the copper from the filtrate as above.

XII. MERCURY.

57. ORES.

Cinnabar, HgS, with 86.2 Hg; *native mercury*, *mercurial tetrahedrites*, with 0.5 to 17 per cent. Hg.

58. FIRE ASSAYS.

The object of these assays is to separate the sulphur, either by union with alkalies, iron, lime, etc., or to oxidize it by means of lead oxide, by heating the ores in retorts, tubes, or crucibles, and condensing the mercurial vapors liberated into liquid mercury, which is weighed either by itself, or, what is more accurate, in combination with gold. In smelting works, where many assays have to be made, small distilling furnaces[1] are generally on hand for this purpose. Notwithstanding the defects of the fire assays, it has not been possible to replace them by simple *wet* methods.[2]

A. Assays yielding free mercury. — 140 to 1800 grammes (2160.53 to 27,778.23 grains), according to richness, of cinnabar ore, are heated with one-half or equal parts of black flux, or 50 per cent. iron filings, or 30 per cent. lime, and 30 per cent. powdered wood charcoal, either in clay or iron retorts, in the latter case without iron filings (native mercury ore, almagam, etc., it is best to heat in glass retorts), at a slowly increasing heat, in a suitable furnace (Figs. 34 to 36, pp. 62, 63). The vapors are condensed in the receivers represented by Figs. 34 to 36, or in a wet linen bag tied to the end of the stem of the retort, the lower part of the stem being at the same time kept cool by moist strips of linen or paper tied around it. The mercury adhering to the neck is removed by gently tapping and wiping out, and that from the receiver is dried with absorbent paper and caustic lime, and weighed in a watch-glass.

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[1] B. u. h. Ztg. 1854, p. 394 (Idria).

[2] Muspratt's Chem. v. 1296. Mohr, Titrirmethode, 1874, pp. 236, 318, 441, 438.

Idria:[1] 140 grammes (2160.52 grains) of ore, with two or three spoonfuls of powdered lime, are placed in iron distilling tubes of about 52 millimeters (2.04 inches) diameter, lying in two rows, one above the other, on each side of a furnace. The receivers are luted on, and the process is finished when the tubes show a bright-red heat. The loss of mercury is considerable.[2] *Hungarian mercurial tetrahedrite:*[3] The ores are heated with the same quantity of iron turnings—roasted ore at the same time with an equal quantity of lead oxide[4]—in glass retorts resting upon clay dishes. The neck of the retorts, when the operation is finished, are broken off by a blow, and the mercury is removed by means of a wiper of rabbit fur. It is then collected into a globule and weighed. *Rose's* method: A body of magnesite (or chalk with an equal quantity of sodium bicarbonate), 26 to 52 millimeters (1.02 to 2.04 inches) long is introduced into a glass tube, closed at one end, and measuring 314 to 470 millimeters (12.36 to 18.5 inches) in length, and 9 to 13 millimeters (0.35 to 0.51 inch) in width. Upon this is placed an intimate mixture of the ore and quicklime in excess, upon this more lime with which the mortar has been cleaned off, then more quicklime, and upon all a loose plug of asbestos. The open end of the glass tube is drawn out and bent to an obtuse angle, and introduced into a narrow-necked flask, so that its end just touches the water contained therein. The horizontal part of the tube is gradually heated from front to back in a *combustion furnace*, such as is used for organic analyses (Fig. 58, without the cylinder on the right). When the operation is finished, the bent end of the tube, in which the mercurial vapors have been condensed, is cut off, and the mercury, which has been protected from oxidation by the current of carbonic acid which is developed, is collected in the matrass. This is well shaken and allowed to settle. The clear water is then poured off, and the mercury placed in a previously weighed porcelain crucible. The water still adhering to it is removed with blotting paper. It is then dried under a bell-glass over sulphuric acid, or in an air-bath at 100° C. (212° F.), and weighed.

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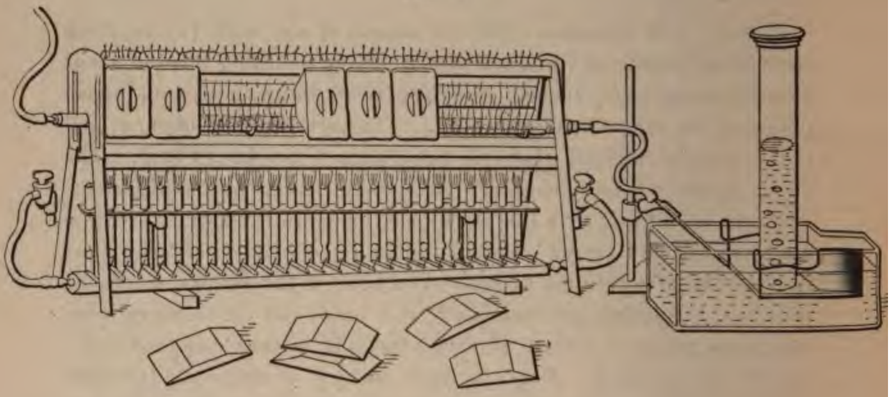
[1] B. u. h. Ztg. 1854, p. 394.

[2] B. u. h. Ztg. 1854, 357.

[3] B. u. h. Ztg. 1866, pp. 24, 262.

[4] Bergwerksfreund, v. 127 (Berthier). B. u. h. Ztg. 1879, p. 206 (Atwood).

Fig. 58.



B. Assays in which the mercury is determined in combination with gold.—These are the most accurate assays.

1. *Eschka's process.*[1]—The quantity of ore taken for the assay varies according to its richness. If the ore carries as much as 1 per cent. 10 grammes (154.32 grains), 1 to 10 per cent. 5 grammes (77.16 grains), and over 10 per cent. 2 grammes (30.87 grains) are used. The sample is placed in a porcelain crucible, the edge of which has been ground smooth, and mixed with half its quantity of iron filings free from grease, covered with a layer of iron filings 5 to 10 millimeters (0.19 to 0.39 inch) thick. A well-fitting concave cover, made of fine gold, and previously accurately weighed, and the concavity of which is filled with distilled water, is now placed on the crucible.

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[1] Oestr. Ztschr. f. Berg. u. Hüttenwes. 1872, No. 9. B. u. h. Ztg. 1872, p. 173.

The lower part of the crucible is heated by a flame for about 10 minutes, during which time the mercury is volatilized, and deposits itself on the gold. The gold cover is now removed, the water in its concavity poured off, and the mirror of mercury washed with alcohol. The cover is then dried for about two or three minutes in the water-bath, placed upon a tared porcelain crucible and allowed to cool in the desiccator, and then both the mercury and crucible are weighed together. The most accurate results are obtained in the case of poor ores carrying up to 10 per cent. Hg.

2. *Küstel's assay.*[1]—This is executed in a manner similar to the above, before the blowpipe, with the difference that the heating is done in a tube, the front end of which is provided with a gold spiral.

C. Assay of cinnabar.—10 grammes (154.32 grains) of cinnabar ore are introduced into a glass retort (Fig. 35, p. 63), and heated. The sublimate of mercury sulphide which deposits itself in the neck of the retort is collected and weighed. Some metallic mercury freed by organic substances, which may have been present, may be mixed with the sublimate. This is removed from the sublimate by nitric acid, and the quantity of mercury dissolved ascertained by the difference in weight. 86 parts of mercury correspond to 100 parts of cinnabar.

59. WET ASSAYS.

These may be—

A. Gravimetric assay.—1 gramme (15.43 grains) of cinnabar is heated with *aqua regia*, and repeatedly evaporated with hydrochloric acid, in order to expel the nitric acid. The solution of chloride is boiled with stannous chloride in excess, the clear fluid is poured off, and the beads of metal are collected into a coherent globule, by heating it again with some stannous chloride and a few drops of hydrochloric acid. The mercury is then washed by decantation, first with water containing hydrochloric acid, and then with pure water. It is now introduced into a small porcelain crucible, previously weighed, and the greatest part of the adhering water removed by means of filtering paper. The mercury is then dried in a desiccator (Fig. 17*a*, p. 43), with concentrated sulphuric acid, and weighed.

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[1] B. u. h. Ztg. 1874, p. 70.

B. Volumetric assays.[1]—These are mostly complicated, and possess no advantage over the ordinary analytical determination by weight, or, are not generally available, as they require the absence of certain metals.

XIII. ANTIMONY.

60. ORES.

Stibnite (*antimony sulphide*), Sb_2S_3, with 71.77 Sb; *valentinite* (*antimony oxide*), Sb_2O_3, with 83.56 Sb; *pyrostilbite* (*antimony oxysulphide*), $Sb_2O_3.Sb_2S_3$, with 77.21 Sb.

61. FIRE ASSAYS.

The assays of antimony sulphide, which is the principal ore, are inaccurate on account of the volatilization of antimony, incomplete decomposition by alkaline carbonates and even by potassium cyanide (4 parts), as well as on account of iron, which always passes partly into the antimony. There are likewise no simple docimastic tests by the *wet method.*[1] Sometimes the yield of antimony sulphide (*antimonium crudum*) contained in the ore is ascertained by the liquation process, by an assay on a small scale.

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[1] Mohr, Titrirmethode, 1874, pp. 236, 318, 436, 438, 441. Fresenius' Ztschr. ii. 381.

A. Liquation process for determining antimonium crudum.—1 to 1½ kilogrammes (2.2 to 3.3 lbs.) of ore comminuted to fragments the size of a hazel-nut or walnut are introduced into a covered crucible having a perforated bottom and fitting air-tight in another crucible in such a manner that sufficient space is left between the two to allow the fused antimony sulphide to collect in the lower crucible. The lid and the joint between the two crucibles should be luted with fire-clay and sand. The lower crucible is surrounded with some poor conductor of heat (ashes), and the upper ore with live coals, kept in a glow with a bellows, and heated to a moderate red heat. The antimony sulphide will melt and collect in the lower crucible.

B. Determination of antimony in antimony sulphide.

1. *Assay by precipitation.*—5 grammes (77.16 grains) of ore are fused in a crucible with the same or double the quantity of black flux, or potassium carbonate and flour, about 2 grammes (30.87 grains) of iron filings, 0.75 to 1.25 grammes (11.57 to 19.29 grains) of borax-glass, and a cover of common salt. The fusion is continued for three-quarters of an hour. When the operation is finished, the brittle regulus is freed from slag, and the adhering particles of slag are removed by washing. The yield by this assay is about 68 per cent., and if more

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[1] Fresenius' Ztschr. xvii. 185 (Becker's gewichtsanalytische Probe); Mohr, Titrirmethode, 1874, p. 267, 309; Muspratt's Chemie, i. 820; Fleischer, Titrirmethode, 1876, p. 299.

iron is added, it will appear to be larger on account of the contamination of the antimony by iron.

5 grammes (77.16 grains) of antimony ore are mixed in a crucible (Fig. 39, p. 66) with 10 grammes (154.32 grains) of anhydrous potassium ferrocyanide. The mixture is covered with 2.5 grammes (38.59 grains) of potassium cyanide and heated to a cherry-red heat. The yield is 72 per cent.[1]—*Or:* 10 grammes (154.32 grains) of ore, and 40 to 50 grammes (617.29 to 771.62 grains) of potassium cyanide, with a covering of common salt, are fused at a high temperature.—*Or:* 100 parts of antimony sulphide, 42 parts of iron filings, 10 parts of sodium sulphate, and 2 parts of powdered wood charcoal are fused. Yield 62 per cent. antimony.—*Or:* 100 parts of antimony sulphide, 80 parts of iron slag, 50 parts of sodium carbonate, and 10 parts wood charcoal. Yield 60 per cent. Impure buttons are comminuted and treated with concentrated nitric acid, filtered, the precipitate of antimonic acid washed, dried, and ignited in a porcelain crucible. It is then weighed, and the weight found multiplied by 0.7922 gives the metallic antimony.

2. *Roasting and reducing assay.*—The ore, which is very fusible, is carefully roasted at a very gradually rising temperature until a yellowish-white powder has been formed. This is fused for about three-quarters of an hour with the same or double the quantity of black flux, or potassium carbonate and flour, with a cover of common salt. If necessary some borax is added. The yield will be at the utmost from 64 to 65 per cent. Sb. *Oxidized ores* do not require roasting, and are fused with 3 parts of black flux (with 1 part of argol), 1 part of sodium carbonate, and 15 per cent. of powdered wood charcoal, at not too high a temperature: or, 10 grammes (154.32 grains) of ore with 25 grammes (385.80 grains) of black flux and 1 part of argol with a cover of salt.

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[1] B. u. h. Ztg. 1856, p. 319.

62. WET ASSAYS.

Namely:—

1. *Gravimetric assay.*—0.5 gramme (7.71 grains) of antimony sulphide is dissolved in *aqua regia*, some tartaric acid is added, and the solution is filtered. The filtrate is saturated with ammonia and an excess of yellow ammonium sulphide, and digested for some time on the water-bath. It is then filtered, but without bringing the precipitate upon the filter. This is again digested with ammonium sulphide and then filtered. The antimony sulphide is thrown down out of the filtrate by the addition of diluted hydrochloric acid. The sulphuretted hydrogen is driven off on the water-bath, and the liquid then filtered upon a filter, previously dried at 100° C. (212° F.), and weighed, washed with sulphuretted hydrogen water, the precipitate dried at 100° C. (212° F.) until the weight remains constant. A part of the contents of the filter is then weighed off in a small porcelain boat, placed in a glass tube, and heated in a current of carbonic acid gas (Fig. 58, p. 230), in order to remove the sulphur in excess, until no more of the latter escapes. The Sb_2S_3, containing 71.8 per cent. Sb, is weighed, and from this the antimony contained in the entire mass in the filter is calculated.

2. *Volumetric method.*—The antimony sulphide is dissolved in hydrochloric acid, and heated until the odor of sulphuretted hydrogen can no longer be detected. Tartaric acid, or potassium-sodium tartrate, is added, and the solution supersaturated with a cold, saturated solution of sodium bicarbonate in the proportion of about 20 cubic centimeters (1.22 cubic inches) to 0.1 gramme (1.54 grains) of Sb_2O_3. The result will be a solution, which, on the addition of iodine, will be converted into antimonic acid

and hydriodic acid, $SbHO_2+2I+H_2O=SbHO_3+2HI$. Starch solution is now added, and a sufficient quantity of titrated solution of iodine to color the fluid blue is allowed to drop into the solution from a burette. A decinormal solution of iodine is prepared by dissolving 12.7 grammes (196 grains) of iodine in potassium iodide, and diluting this to the bulk of 1 liter (1.76 pint). 2 atoms of consumed iodine correspond to 1 molecule of antimony oxide, or 1 cubic centimeter (0.061 cubic inch) of solution of iodine to 0.0061 gramme (0.09 grain) of antimony. The standard of the solution of iodine is determined by titration with tartar emetic, observing the same conditions regarding the concentration and quantity of the reagents (tartaric acid, sodium hydrocarbonate, etc.) in the subsequent titration.

See "XVIII., Sulphur," concerning the indirect determination of antimony in Sb_2S_3 by the quantity of sulphuretted hydrogen evolved therefrom.

XIV. ARSENIC.

63. ORES.

Native arsenic, *mispickel*, FeAsS, with 46 As; *leucopyrite*, Fe_2As_3, with 66.8 As; nickel and cobalt ores, etc.

64. FIRE ASSAYS.

The object of these is to determine the quantity of arsenic, or of its compounds, which may be obtained from the ores.

A. Native arsenic.—300 to 500 grammes (4629.70 to 7716.17 grains) of mispickel or leucopyrite (when arsenious acid is present the ores are mixed with 16 to 20 per cent. powdered charcoal, and with potassium carbonate in case metallic sulphides should be contained in the ore) are introduced into a clay tube, one end of which is closed. A spiral of sheet iron is placed in the open end, and the tube is closed by a sheet-metal cap, which is loosely luted on. The tube is then brought into the furnace, and the charge is gradually heated for one to one and a half hours to a red heat, the end with the spiral projecting from the furnace. When the operation is finished, the tube is allowed to cool, and taken out. The sheet-iron spiral is then taken out and unrolled, and, if the operation has been conducted at the proper temperatures, scales of white, flaky arsenic and some gray powder, both allotropic modifications of arsenic, will fall off. The product is then weighed ($FeAsS = FeS + As$ and $Fe_2As_3 = 2FeAs + As$).

White metallic scales will be the result, when the receiver is small and has nearly the same temperature as that of the arsenical vapors; and *gray* powder, when the receiver is large or has a decidedly lower temperature than that of the arsenical vapor, and when it is evolved along with other heated gases (as in the reduction of arsenious acid by charcoal).

B. Arsenious acid.—2 to 5 grammes (30.87 to 77.16 grains) of ore are placed in the open end of a refractory glass tube, the other end of which, somewhat drawn out and bent in a right angle, projects into a large *Woulff* bottle. The end of the tube containing the ore is laid so as to incline somewhat upwards, in a combustion furnace (Fig. 58, p. 230), and heated. The *Woulff* bottle is connected with an aspirator, when the arsenious acid will deposit itself in the straight and curved part of the tube, and in the *Woulff* bottle. It is driven by heating, from the horizontal to the bent part of the tube; this is cut off, the arsenious acid is wiped out with a feather, and then weighed together with that contained in the bottle.

C. Realgar (*red orpiment*), with 70.03 As, and *yellow orpiment*, As_2S_3, with 60.9 As.—The object of the docimastic tests is to determine the quantity of orpiments which can be prepared from the raw materials in question, or to ascertain the proportions of these to be added in certain technical processes.

1. *Assays for the determination of realgar.*—Iron pyrites ($7FeS_2=FeS_2+6FeS+6S=23$ per cent. S) and arsenical pyrites ($FeAsS=FeS+As=46$ per cent. As) in different proportions (20 to 30 grammes=308.64 to 462.97 grains, or more) are heated in a glass tube closed at one end, or in a glass retort, whereby realgar is sublimed. This is fused in a porcelain crucible, and its color examined. Lighter or darker shades can be given to the color by adding, respectively, sulphur or arsenic.

2. *Assays for the determination of yellow orpiment.*—A mixture of arsenious acid with sulphur (together 10 to 20 grammes, 154.32 to 308.64 grains) in different proportions is heated (generally with 6 to 12 per cent. of sulphur, or less) in a glass retort at a gradually rising temperature, until the sublimation of the yellow product is complete.

While the *native yellow orpiment* is a combination of As_2S_3, difficult to dissolve in acids, the *artificial* product consists principally of arsenious acid colored by a few per cent. of arsenic sulphide, and is consequently very poisonous.

65. WET ASSAYS.

These may be—

A. Gravimetric assays.

1. *Wet assay.*—½ to 1 gramme (7.71 to 15.43 grains) of ore is ignited in a porcelain crucible at a strong red heat, with 4 to 5 times the quantity of saltpetre, and 1½

times the quantity of calcined sodium carbonate, with a thick covering of these fluxes. When the crucible is cold, the potassium arseniate is extracted by lixiviation with hot water, and evaporated to dryness with nitric acid. The dry mass is treated with water, the silicic acid filtered off; the filtrate is treated with ammonia in excess, then with a solution of magnesium sulphate (or at once with magnesia mixture prepared from 110 parts of crystallized magnesium chloride, 700 parts concentrated ammonia, 140 parts ammonium chloride, and 1300 parts water). The liquid is allowed to stand for 12 hours, the ammonium-magnesium arseniate, $2(MgNH_4.AsO_4)+H_2O$, is filtered off upon a filter previously dried at 100° C. (212° F.), and weighed; 100 parts of salt dried at 100° C. (212° F.) and weighed, will contain 60.51 parts of arsenic acid, corresponding to 65.21 per cent. of arsenic and 86.08 per cent. of arsenious acid. By igniting *very carefully* and not too quickly, the magnesium salt passes into $Mg_2As_2O_7$. Or the sample is digested in strong nitric acid with the addition of a few crystals of potassium chlorate. The solution is diluted with water and filtered. Some lead nitrate in solution is added to the acid liquid, when lead sulphate will be separated, lead arseniate remaining in solution. The precipitate of lead sulphate is filtered off, the filtrate saturated with soda, when the lead arseniate will be separated. This is filtered off, washed, dried, and weighed. 100 parts arseniate = 22.2 parts of metallic arsenic, or 29 parts of arsenious acid.

2. *Wet method combined with the dry.*[1]—1 to 1½ grammes (15.43 to 23 51 grains) of the substance is fused in the manner indicated under 1, with saltpetre and sodium carbonate, in order to obtain a solution of alkaline

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[1] Plattner-Richter's Löthrohrprobirkunst, 1878, p. 651.

arseniate. The filtrate is saturated with nitric acid, and strongly diluted in case sulphuric acid is present. Silver nitrate in excess is then added, and sufficient ammonia to cause the precipitate to disappear. The excess of ammonia is evaporated without boiling until its odor has disappeared. The silver arseniate is then filtered off, dried, and smelted with lead, and the arsenic calculated from the quantity of silver found, 1 atom of arsenic being precipitated to 3 atoms of silver, or 100 silver corresponds to 23.15 arsenic = 35.5 arsenic acid.

B. Volumetric assays.—The method most used is *T. Mohr's*[1] *estimation of arsenious acid;* according to which arsenious acid combined with soda is completely converted into arsenic acid by iodine ($As_2O_3 + 2I_2 + 2Na_2O = 4NaI + As_2O_5$).

A solution containing in 500 cubic centimeters (30.5 cubic inches) 2.5 grammes (38.58 grains) of iodine and 4 grammes (61.73 grains) potassium iodide, or in 1 c.cm. 0.005 gramme (0.077 grain) of iodine, is added to a solution containing sodium arsenite, sodium bicarbonate, and some starch paste. Fixing of the standard: 4.95 grammes (75.38 grains) of arsenious acid are placed in a flask and dissolved in sodium bicarbonate, in about 200 cubic centimeters (12.2 cubic inches) of water. The clear solution is poured off, and sodium salt and water are added in small portions until solution is complete. It is then transferred to a liter flask, 20 to 25 grammes (308.64 to 385.80 grains) more of sodium bicarbonate are then added, and the flask is filled up to the mark. 10 c.cm. of this solution are taken, some fresh starch solution and sodium bicarbonate added, the liquid diluted to about 150 c.cm., and then titrated with the solution

[1] Mohr. Titrirmethode, [illegible]

of iodine until the blue color appears, which must not disappear even when sodium bicarbonate is added. *Arsenic acid* must be reduced to arsenious acid by introducing sulphurous acid gas into the hot acid solution, or by the addition of sulphites.

XV. URANIUM.

66. ORES.

Pitch blende, Ur_3O_8, with 84.9 Ur.

67. WET ASSAYS.

Namely:—

A. Gravimetric assays.

1. *More accurate analytical process.*—1 to 2 grammes (15.43 to 30.87 grains) of ore, etc., are decomposed with concentrated nitric acid. The solution is diluted and the residue and precipitate (silicic acid, lead sulphate, basic antimony and bismuth salts) are filtered off. The arsenic acid in the filtrate is reduced by means of sulphurous acid to arsenious acid, and the sulphurous acid removed by boiling. It is then precipitated with sulphuretted hydrogen (As, Sb, Pb, Bi, Cu), filtered, and the sulphuretted hydrogen removed by boiling. The iron is then oxidized by potassium chlorate, ammonium carbonate in excess added, and the liquid filtered. Ammonium sulphide is now cautiously added in the cold in order to precipitate Mn, Zn, Ni, Co, leaving the uranium in solution. The liquid is then filtered, and the filtrate heated with nitric acid to separate sulphur. It is now again filtered, d when the solution has become cold, the uranium is precipitated, as brownish-yellow ammonio-uranic oxide,

by ammonia. This is filtered off, washed, dried, and ignited to green uranoso-uranic oxide ($UrO_2.2UrO_3 = Ur_3O_8$), with 84.8 uranium, corresponding to 96.22 uranous oxide (UrO_2) and 101.9 uranic oxide (UrO_3).

2. *Patera's technical test.*[1]—5 grammes (77.16 grains) of ore are dissolved in nitric acid, not in excess. The unfiltered solution, which has been freed from the excess of nitric acid by boiling, is super-saturated with sodium carbonate, boiled for a short time, and the solution containing the sodic-uranic carbonate is filtered into a golden dish. The solution is evaporated to dryness, the residue ignited and extracted with hot water, and the insoluble acid sodium uranate ($Ur_4Na_2O_7$) is filtered off, ignited, and weighed. 100 parts of the weight obtained equals 88.3 parts of uranoso-uranic oxide.

In case a golden capsule should not be at hand, the solution of the uranic oxide in soda is treated with sodium hydrate in order to precipitate hydrated acid sodium uranate. It is then filtered, washed, and dried, and the precipitate is removed as much as possible from the filter and ignited together with the ash of the filter. It is then again washed upon the filter and dried and ignited. In case a considerable quantity of copper is present, a small quantity of it passes into the alkaline solution.

B. Volumetric assay.[2]—1 to 2 grammes (15.43 to 30.87 grains) of ore is dissolved in concentrated sulphuric acid. The sulphuric acid (not hydrochloric acid) solution is diluted according to the richness of the ore, to $\frac{1}{2}$ or $\frac{1}{4}$ liter (0.88 to 0.44 pint). 50 cubic centimeters (3.05 cubic inches) of this are taken, placed in a suitable flask, and diluted with 100 cubic centimeters (6.1 cubic inches) of water. The liquid is boiled for half an hour with zinc until the yellow solution of uranic oxide has assumed the sea-green color of uranous oxide. All the zinc is dissolved, and the uranous oxide is titrated with potassium permanganate (p. 127). Uranous oxide requires the same quantity of potassium permanganate to become oxidized, as ferrous oxide.

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[1] Dingler, clxxx. 242 (Patera). Fresenius' Ztschr. v. 229 (Fresenius); viii. 387 (Winkler).

[2] Journ. f. prakt. Chem. xcix 231 (Belohoubeck). Fresenius' Ztschr. xi. 179 ; xvi. 104.—Gouyard's Probe in Chem. Centr. 1864, p. 339.—Analyse der Uranoxydalkalien in Fresenius' Ztschr. iii. 71 (Stolba).

XVI. CHROMIUM.

68. ORES.

Chrome iron ore, Cr_2FeO_4, with 30 to 65 Cr_2O_3; *crocoisite* (*red lead ore*), $Pb.CrO_4$, with 30.96 CrO_3.

69. WET ASSAYS.

Volumetric assays are less frequently made use of than gravimetric assays, and the latter vary, especially in the manner in which the very difficultly decomposable chrome iron-ore is decomposed.

A. Gravimetric assays.[1]

1. *Direct assay.*—According to *Pourcel's* method: 2 grammes (30.87 grains) of the ore in coarse powder are highly heated in order to facilitate its comminution. It is then ground in an agate mortar, or on a porphyry plate, to an impalpable powder, which should show no glistening particles. This powder is heated to 120° C. (248° F.) until it loses no more in weight, and then a sample

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[1] Journ. f. prakt. Chem. lvii. 256 (Calvert). Fresenius' Ztschr. i. 497 (O'Neill, Oudesluys, Genth); iv. 63 (Souchay); 1861, p. 34 (Mitscherlich); 1870, p. 71 (Storer). Polyt. Centr. 1856, p. 701 (Hart). Dingler, cxciii. 33 (Clouet); cxcvii. 503 (Britton); ccxxi. 450 (Dittmar); ccxxiv. 86 (Fels). Bullet. de la soc. de l'industr. minér., St Etienne, 1878, livr. iv. p. 867. (Pourcel).

of 0.5 gramme (7.71 grains) is quickly weighed off. 5 grammes (77.16 grains) of sodium carbonate are introduced into a platinum crucible and heated in the mouth of the muffle in order to dry it, but not sufficiently to fuse it. The ore is then intimately mixed in an agate mortar, with 0.5 gramme (7.71 grains) of saltpetre and the warm sodium carbonate until the mixture assumes a uniform color. It is then placed in a platinum crucible and strongly heated, first at the front of the muffle, and then at the back, at a white heat for three hours. The crucible is then taken out, wiped off after it has become cold, and placed in a porcelain dish containing 0.5 liter (0.88 pint) of distilled water which completely impregnates the contents of the crucible. This is allowed to stand for about twelve hours on a sand-bath, at a temperature somewhat less than 100° C. (212° F.). It is then filtered on a very small filter, and the crucible and dish are washed out with hot distilled water. The filtrate containing the potassium chromate and sodium-potassium aluminate is weakly acidulated with sulphuric acid, ammonia in excess is added, and it is then heated to nearly 100° C. (212° F.) for at least three hours. The alumina is then filtered off, the filtrate is introduced into a capacious flask, hydrochloric acid strongly in excess and 100 cubic centimeters (6.1 cubic inches) of pure alcohol of 40° are added, the contents of the flask then agitated and its neck closed by inserting the neck of a smaller flask into it. The liquid is now heated to nearly 100° C. (212° F.) for about forty-eight hours, until the reduction of chromic acid to chromic oxide is complete (whereby the liquid assumes an emerald-green color), and the odor of alcohol has disappeared. Ammonia in excess is then added, the liquid is allowed to stand for about twelve hours at a temperature of nearly 100° C. (212° F.), so that bubbles are formed on the sides of the flask. The precipitate of hydrated chromic oxide is filtered on a small filter, washed with boiling, slightly ammoniacal water, and dried. The chromic oxide is then ignited and weighed.

According to *Fels*, *Calvert's*, *Britton's*, and *Dittmar's* are the best methods for decomposing chrome iron ores.

2. *Indirect assay.*[1]—The ore is fused with potassium nitrate and sodium carbonate (in the same manner as arsenic, p. 238), and the alkaline chromates are lixiviated. The solution is saturated with acetic acid, and boiled, in order to remove the carbonic acid. It is then diluted with water (to prevent a separation of silver acetate), and a sufficient quantity of silver nitrate is added. The precipitate of silver chromate will then contain to one atom of chromium one-half atom of silver (100 $Ag = 48.69\ Cr = 70.92\ Cr_2O_3 = 93.15\ CrO_3$). The precipitate, together with the filter, is boiled in strongly diluted hydrochloric acid, the silver chloride formed is filtered off, smelted with lead, and cupelled, and the chromium calculated from the resulting quantity of silver.

B. Volumetric assay.—1 gramme (15.43 grains) of the ore is powdered and ground as fine as possible. It is then fused with soda and saltpetre and converted into alkaline chromate (p. 244). It is then supersaturated with sulphuric acid and a weighed quantity of pure ferrous sulphate or ammonio-ferrous sulphate, when, the ferrous oxide becoming oxidized at the cost of the chromic acid, the latter is transformed into chromic oxide, and the color of the reddish-yellow solution becomes distinctly green ($2CrO_3 + 6FeSO_4 + 6SO_3 = Cr_2S_3O_{12} + 3Fe_2S_3O_{12}$); therefore, 6 equivalents of FeO correspond to 2 equivalents $CrO_3 = 3 : 1$. The residue of ferrous oxide which has not been decomposed is titrated with solution of potassium permanganate, when the final reaction will be the more distinct the stronger the liquid has been acidulated with sulphuric acid, which causes the green color of the chromic oxide to become pale.

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[1] Plattner-Richter's Löthrohrprobirkunst, 1878, p. 651.

XVII. MANGANESE.

70. ORES.

Pyrolusite, MnO_2, with 62.8 Mn and 37.2 O; *braunite*, Mn_2O_3, with 69.23 Mn and 30.77 O; *hausmannite*, $MnO.Mn_2O_3$, with 71.7 Mn and 28.3 O; *manganite*, $Mn_2O_3+H_2O$, with 89.9 Mn_2O_3 and 10.1 H_2O; *varvicite*, $(Mn_2O_3+H_2O)+2MnO_2$, with 14.23 MnO, 80.79 O, and 4.98 H_2O; *psilomelane*, $(Mn,Ba,K_2,Li_2)O+4MnO_2$, with 30 to 60 MnO_2; *wad*, $MnO.2MnO_2+3H_2O$.

71. ASSAYS OF PYROLUSITE.[1]

The percentage of manganese in an ore, which is of interest to the iron manufacturer, is generally determined by chemical analysis. *Tamm*[2] has given a process of preparing *manganese regulus* from pyrolusite; while the value of an ore for other technical purposes (manufacture of chlorine and of chloride of lime, the preparation of oxygen) is judged—

1) By the *quantity of chlorine* which the ore yields on treatment with hydrochloric acid $MnO_2+4HCl=MnCl_2+2H_2O+Cl_2$ (81.6 per cent Cl), or, with common salt and sulphuric acid $MnO_2+2NaCl+2H_2SO_4=MnSO_4+Na_2SO_4+2H_2O+2Cl$ (81.6 per cent).

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[1] Muspratt's Chem. [illegible]

[2] Dingler, Bd. [illegible] 1873, p. [illegible]

If an ore contains ferrous oxide, for instance in the form of spathic or magnetic iron, a part of the chlorine evolved from the hydrochloric acid is consumed in the higher oxidation of the ferrous oxide, and is therefore lost for technical use. Only so much of the chlorine as is actually obtained from pyrolusite, is of value to the buyer, and the assays which give this (for instance, *Bunsen's* and *Gay-Lussac's*) are to be preferred to those which give the total amount of chlorine without taking into consideration that, when ferrous oxide is present, the chlorine is not all available for practical purposes.

2. By the *quantity of oxygen* the pyrolusite yields when ignited or treated with sulphuric acid ($MnO_2+SO_3=MnSO_4+O=18.3$ per cent.).

3. By the *foreign admixtures* according to their quality and quantity. *Substances soluble in acids* (for instance, calcium and iron carbonates) are especially injurious. They increase unnecessarily the cost of manufacturing chlorine, and, by evolving considerable quantities of carbonic acid, exert a disturbing influence on the preparation of chloride of lime. For this reason, the quantity allowed is sometimes limited by contract to one per cent.

The quantity of acid required for the decomposition is determined by finding the quantity of pure marble dissolved by a given quantity of hydrochloric acid; then allowing the same quantity of acid to act on a known quantity of the ore; then when chlorine ceases to be evolved, introducing the marble, and when the evolution of carbonic acid has ceased, removing the marble and weighing. The quantity of acid is ascertained from the difference in the loss of marble in the two cases. 100 parts of marble saturate 70.5 parts of dry and 205 parts of aqueous hydrochloric acid of 1.17 specific gravity; and when the acid is of 1.09 specific gravity, corresponding to 18.2 per cent. of dry acid, 7.3 milligrammes (0.10 grain) of dry acid correspond to 1 gramme (15.43 grains) of dissolved marble.

4. *By the decomposability and the physical condition of the ore*, as they require different quantities of acid, for instance, *Spanish* ore more than *Nassau* ore.

Hydrochloric acid dissolves the ferrous oxide contained in manganese ores more readily than sulphuric acid, and differences may, therefore, arise in the yield of available chlorine from an ore, according as one or the other acid has been used, since the more ferrous oxide dissolved, the more chlorine is kept back (p. 247).

5. By the *constitution* of the ore, which requires also different quantities of acid.

1 atom pyrolusite requires 4 atoms hydrochloric acid to yield 2 atoms of chlorine ($MnO_2 + 4ClH = MnCl_2 + Cl_2 + 2H_2O$); while braunite requires 6 atoms of the acid ($Mn_2O_3 + 6ClH = 2MnCl_2 + Cl_2 + 3H_2O$).

6. By the *amount of hygroscopic water*, which is sometimes considerable, and must be removed by drying, for instance, upon *Fresenius'* disk (Fig. 2, p. 26), at 100° or 110 to 115° C. (212° or 230 to 239° F.).

It is customary to represent the commercial value of manganese ores, whether the available chlorine or oxygen is to be ascertained, in terms of manganese peroxide equivalent to the chlorine or oxygen yielded (even if the ore does not contain it, as, for instance, braunite); namely, 2 atoms of chlorine (17), or 1 atom oxygen (16) = 1 atom peroxide. Frequently 60 per cent. of peroxide is taken as the standard in commerce, and from a fixed price for this, the value of the ore is determined according to the higher or lower percentage of peroxide it contains.

The following Table gives the theoretical yield of oxygen, chlorine, and peroxide of the different ores:—

	Oxygen per cent.	*Chlorine* per cent.	*Peroxide* per cent.
Pyrolusite . . .	18	81.2	100
Braunite . . .	10	45.1	55.5
Hausmannite . . .	6.8	30.6	37.7
Manganite . . .	9	45.6	50.
Varvicite . . .	13.8	62.2	76.6

A. Gravimetric assays.—These require but simple utensils, and can be easily executed by not very experienced operators, but the results, if certain substances are present, are inaccurate, or require control assays.

1. *Method of Fresenius-Will.*[1]—2 to 5 grammes (30.87 to 77.16 grains) of very finely powdered ore are weighed out and placed in the flask *A* (Fig. 59), made of thin glass, and capable of holding about 120 cubic centimeters (7.32 cubic inches). To this are added two and a half times the quantity of powdered neutral potassium oxalate (5 to 12.5 grammes; 77.16 to 192.90 grains), and the flask is then filled to about one-third with water. The flask *A* is hermetically connected by the tube *c* (corks saturated with wax or paraffine, or caoutchouc stoppers should be used) with the flask *B*, half filled with English sulphuric acid. The tube *a* is closed with a plug of wax, or a caoutchouc tube with a glass rod, and the whole apparatus is weighed. The air is then aspirated at *b*, in order to create a partial vacuum in the flask *B*, by which the air above the liquid in flask *A* will likewise be somewhat rarefied, in consequence of which the acid

Fig. 59.

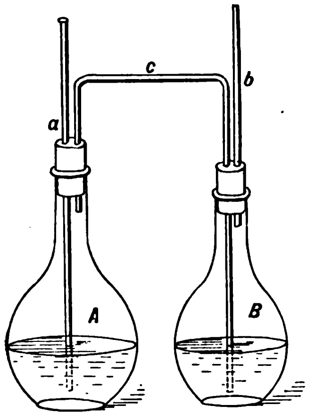
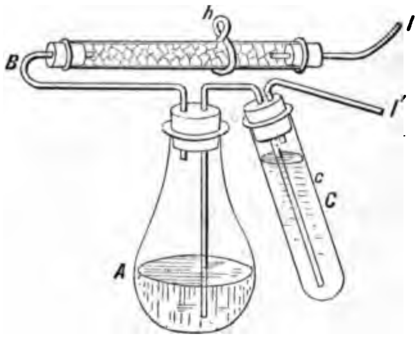


Fig. 60.



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[1] Ann. der Chemie u. Pharm. xlix. 137. Fresenius' Ztschr. i. 48 (Röhr); i. 110 (Kolb); i. 81, 110 (Kolbe). Dingler, clxxxvi. 210 (Lunge).

from *B* will pass through *c* into *A*, after the suction ceases. Carbonic acid is developed by the action of the sulphuric acid upon the ore and oxalate ($MnO_2+C_2O_3+SO_3=MnSO_4+2CO_2$), which passes through *c* into *B*, is dried in passing through the sulphuric acid, and escapes through *b*. The drawing over of acid by suction is repeated until no more carbonic acid is developed, and no black residuum is observed in *A*, gentle heating being employed towards the last. The plug or stopper is now removed from *a*, suction is applied at *b*, in order to remove the carbonic acid contained in the apparatus. When this is *entirely* cold, the apparatus is weighed, and the percentage of peroxide calculated from the loss of carbonic acid; 2 atoms CO_2 (88) being equal to 1 atom MnO_2 (87.14, or, in round numbers, 87).

If carbonates are present the result will be affected, and the following process becomes necessary to neutralize their influence. A little sulphuric acid is drawn over from the flask *B* into *A*, the latter containing only ore and water. The carbonic acid evolved is removed by aspiration, and the apparatus is weighed, the required quantity of potassium oxalate being weighed along with the apparatus upon the same scale pan. The oxalate is then quickly poured into the flask *A*, and the further operation conducted as above.—According to *Mohr*, a percentage of ferrous oxide[1] in the ore (for instance, magnetic or spathic iron) does not affect the result of the assay, but gives too high a percentage of chlorine for commercial purposes, since a part of the chlorine is consumed in the higher oxidation of the iron.—*Lighter* apparatus than that of *Will* and *Fresenius* is described by *Mohr*, Kolbe, and *Rose* (Fig. 60); *A*, flask for the reception of the ore, potassium oxalate, and water; *C*, glass tube for sulphuric acid, diluted with an equal volume of water; *B*, drying-tube with calcium chloride, supported at *h*. The apparatus is weighed, and then tilted in order to transfer acid from *C* through the tube *c* to *A* (or by aspirating on the calcium chloride tube at l). The carbonic acid developed is allowed to escape through the drying-tube *B*, and finally the carbonic acid is expelled from the apparatus by suction at l'.

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[1] Fresenius' Ztschr. 1869, p. 314 (Mohr); 1871, p. 310 (Luck); Dingler, cxcvii. 422 (Pattinson). B. u. h. Ztg. 1871, p. 312 (Sherer).

2. *Method of Fikentscher-Nolte.*[1]—1 to 5 grammes (15.43 to 77.16 grains) of ore, 8 times the quantity of ferrous sulphate free from ferric oxide, an accurately weighed strip of bright sheet-copper 4 to 5 times the weight of the ore, 30 to 35 cubic centimeters (1.83 to 2.13 cubic inches) of hydrochloric acid of 1.12 specific gravity, and distilled water are placed in a suitable flask provided with a rubber valve (Fig. 10, p. 39). The contents is kept at a boiling heat (at least two hours) until the solution, at first brown, becomes nearly colorless, when the ferric chloride, which was first formed, is reduced to ferrous chloride by the copper, the weight of which correspondingly decreases ($MnO_2 + 2FeCl_2 + 2HCl = MnCl_2 + Fe_2Cl_6 + 2H_2O$; then, $Fe_2Cl_6 + 2Cu = 2FeCl_2 + Cu_2Cl_2$). The flask is then quickly filled with boiled water free from air. The liquid is then poured off, the strip of copper quickly thrown into water, rinsed, and dried with absorbent paper, but without rubbing it; then completely dried at 100° C. (212° F.), allowed to become cold in the desiccator, and then weighed. The percentage of manganese peroxide is calculated from the loss of copper, as, according to the above equation, 2 atoms of dissolved copper (126.8) correspond to 1 atom of peroxide (87.14).

The oxidizing action of the air upon copper must be avoided, as otherwise more would be dissolved than the required quantity. For this reason a flask provided with a rubber-valve should be used, and ferrous sulphate free from ferric oxide. The copper should further be kept constantly covered by the hydrochloric acid, thoroughly boiled water be used, and the copper quickly rinsed off. In case the ore contains ferric oxide, a control assay must be made, as it forms ferric chloride with hydrochloric acid, and this contributes to the solution of the copper. This must be calculated for by treating a quantity of ore equal to that of the principal assay, with hydrochloric acid, but first *without* copper. This is now heated until all the chlorine has been expelled, the weighed copper is now added, and the liquid boiled until it becomes colorless. The loss in weight of copper by ferric chloride alone is now determined, and this is deducted from the loss which takes place in the principal assay.

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[1] Journ. f. prakt. Chem. xviii. 160, 173 (Fikentscher). B. u. h. Ztg. 1859, p. 149; 1864, p. 374 (Nolte).

B. Volumetric assays.—Those methods which give only the actually available chlorine, as *Bunsen's* and *Gay-Lussac's*, deserve the preference, as other methods indicate too large a percentage of chlorine, which, in operations on the large scale where the ore contains ferrous oxide, cannot be depended on.

Perrey[1] found that an ore which gave 100 MnO_2 according to Fresenius' method yielded 99.1 according to *Mohr's*, 100.6 according to *Hempel's*, 97.8 according to *Gay-Lussac's*, and 98.4 per cent. MnO_2 according to *Bunsen's*. The differences are partly explained by the fact that, in making the assays, the action of the ferrous oxide present is taken into consideration in some, while in others it is not; and that, when sulphuric acid is used (*Fresenius*, *Hempel*), or hydrochloric acid (*Bunsen*, *Gay-Lussac*), more or less ferrous oxide is dissolved, as it is not equally soluble in these acids.

1. *Bunsen's method with iodine.*[2]—This is based upon the principle that, when chlorine evolved from manganese ore by hydrochloric acid ($MnO_2 + 4ClH = MnCl_2 + 2Cl + 2H_2O$) is introduced into a solution of potassium iodide, it separates from this a corresponding quantity of iodine, indicated by the appearance of a brown color. After the addition of starch, which colors the solution blue, the quantity of separated iodine is determined by a

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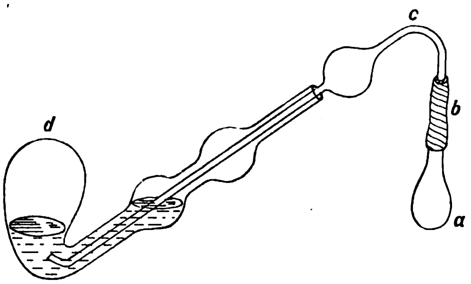
[1] Dingler, ccxxvi. 194.

[2] Mohr, Titrirmethode, 1874, p. 625. Muspratt's Chemie, iv. 1118. Fresenius' Ztschr. 1869, p. 314; 1870, p. 410. Journ. f. prakt. Chem., Neue Folge, xviii. 101 (Marawski und Stingl).

titrated solution of sodium hyposulphite, which is added until the color has disappeared ($2Na_2S_2O_3+2I=Na_2S_4O_6+2NaI$); whence 2 atoms of chlorine correspond to 2 atoms of iodine, and these to 1 atom of manganese peroxide. This assay is very accurate, and the results obtained are not affected by any admixtures, but it requires somewhat skilful manipulation.

The retort *d* (Fig. 61), the neck of which is provided with two bulbs in order to lessen the danger of loss by overflow, is filled one-third full with a freshly prepared solution of one part potassium iodide in ten parts of water.

Fig. 61.



The potassium iodide must not become colored on the addition of acid, as this would indicate the presence of potassium iodate, from which more iodine would be separated by chlorine. The retort is then inverted (see Fig. 61), and a glass tube provided with a bulb *c* is introduced into the neck of the retort. The other somewhat wider end of the glass tube is furnished with a caoutchouc tube *b*, previously boiled in a solution of potassium hydrate. 0.1 to 0.5 gramme (1.54 to 7.71 grains) of very finely powdered ore is poured into the flask *a*. This is then about two-thirds filled with fuming hydrochloric acid, the neck of the flask is quickly pushed into the moistened caoutchouc tube *b*, so that glass touches glass. The flask is now slowly heated over a spirit-lamp, so as to avoid the passage of liquid from *d* back into *a*. The heating is continued until the greenish color of the chlorine in the bulb of the connecting tube disappears, the ore is entirely decomposed, and a peculiar crackling noise is heard in the flask. The heat is somewhat increased for about half a minute after the crackling noise has been perceived, to prevent the liquid, containing about 5 grammes (77.16 grains) of solid potassium iodide and colored brown by the separated iodine, from passing over into the flask. The gas-conducting tube *c* is then withdrawn from the retort with the left hand, the heating of the flask *a* being continued all the while by holding the spirit-lamp below it with the right hand (if these manipulations are not conducted with proper skill, there is danger that the liquid in the retort will pass over). The tube is then washed off in a beaker-glass. The retort, containing the brown iodine solution, is corked, and carefully shaken, so that the solution may take up all the free iodine, during which operation the liquid must not come in contact with the cork. After the fluid has become entirely cold, it is poured out in the beaker-glass. Should the liquid contain any undissolved iodine, a few crystals of potassium iodide must be added before the contents of the retort is emptied into the beaker-glass. It is then diluted to the bulk of one-half liter (0.88 pint). 100 cubic centimeters (6.1 cubic inches) of this are taken, introduced into a separate vessel, and titrated sodium hyposulphite is added to it as long as a red color is still *distinctly* perceptible. About 2 grammes (30.87 grains) of starch liquor are added, and then more sodium hyposulphite, drop by drop, until the blue color which has been formed just commences to disappear. If necessary, the assay may be controlled by titrating back with a normal solution of iodine, until the blue color appears again. The standard solution of sodium hyposulphite is prepared by dissolving 24.8 grammes (382.72 grains) of sodium hyposulphite in water, and diluting the solution to 1 liter (1.76 pints). 0.1 to 0.2 gramme (1.54 to 3.08 grains) of pure iodine is then dissolved in 18 grammes (277.78 grains) of potassium iodide, free from iodic acid, and this solution is also diluted to 1 liter (1.76 pints), when 1 cubic centimeter (0.061 cubic inch) of normal solution of sodium hyposulphite will correspond to 0.0127 gramme (0.19 grain) of iodine contained in 1 cubic centimeter (0.061 cubic inch) of solution, so that equal volumes correspond.

Fig. 62.

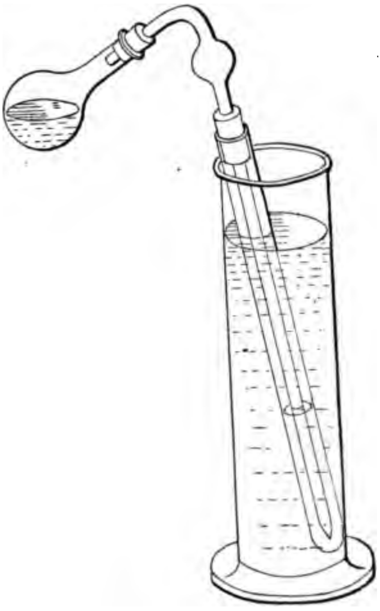


Fig. 62 represents a modified form of this apparatus, in which the bulbed-tube attached to the dissolving flask passes into a long and narrow tube, which is cooled by immersion in cold water, and contains a higher column of potassium iodide solution.

2. *Levol's method with iron.*[1]—0.5 to 0.6 gramme (7.71 to 9.26 grains) of manganese ore, and 0.8 to 1 gramme (12.35 to 15.43 grains) of piano wire (containing on an average 99.6 per cent. of pure iron), are treated with ex-

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[1] Dingler, lxxxv. 299 (Levol); cxcvii. 422 (Pattinson). Fresenius' Ztschr. 1869, p. 509 (Teschemacher u. Smith).

clusion of air with hydrochloric acid, in a flask provided with a rubber valve (Fig. 10, p. 39); when, from the resulting ferrous chloride, a quantity of ferric chloride corresponding to the chlorine developed will be formed ($MnO_2+4HCl=MnCl_2+2Cl+2H_2O$ and $2Cl+2FeCl_2=Fe_2Cl_4$). The liquid is diluted to 0.5 liter (0.88 pint). 100 cubic centimeters (6.1 cubic inches) of this are taken, and, after having become entirely cold, the non-oxidized quantity of ferrous oxide is determined by titration with potassium permanganate (p. 127). The quantity of iron oxidized by the chlorine is determined from the difference; and 2 atoms of iron (112) correspond to 1 atom of manganese peroxide (87.14).

Ammonio-ferrous sulphate, $FeSO_4+(NH_4)_2SO_4+6H_2O$, may be used instead of metallic iron, in the proportion of about 7 grammes (108.02 grains) to 1 gramme (15.43 grains) of manganese ore with 70 per cent. of peroxide, and 8 to 9 grammes (123.46 to 138.89 grains) if the percentage is higher; when 2 atoms of the salt (784) correspond to 1 atom of manganese peroxide (87.14). The assay solution to be titrated should be cold, and strongly diluted, to prevent the hydrochloric acid from being decomposed by the potassium permanganate; or, potassium bichromate[1] may be used instead of potassium permanganate. In this assay (iron test), which is much used in England, a part of the chlorine is consumed for the higher oxidation of the ferrous oxide, if any be contained in the ore.

XVIII. SULPHUR.

72. ORES.

Native sulphur (*sulphur earths*); *iron pyrites*, FeS_2, with 53.33 S and 46.47 Fe; *magnetic iron pyrites*, $5FeS.Fe_2S_3$, with 39.5 S; *copper pyrites*, $CuFeS_2$, with 34.89 S.

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[1] Möhr, Titrirmethode. 1874, p. 632. Polyt. Centrbl. 1871, p. 1117; Oxalsäureprobe in Fresenius' Ztschr. 1870, p. 410.

73. ASSAYS BY DISTILLATION FOR THE DETERMINATION OF THE AMOUNT OF SULPHUR WHICH AN ORE MAY YIELD.

a. *Sulphur earths.*—0.5 to 1 gramme (7.71 to 15.43 ains) of the ore is heated to a strong red heat in an pervious clay retort, on the neck of which is luted a rcelain tube (Figs. 35, 36, p. 63), when the sulphur pors will deposit themselves in the porcelain tube, the d of which just dips in water. The tube is then re-oved and the sulphur collected, dried, and weighed.

Gerlach[1] conducts superheated steam into a glass retort containing e ore, from the neck of which the sulphur, which passes over, drops o a dish containing water.

b. *Iron pyrites.*—2 to 5 grammes (30.87 to 77.16 ains), preferably mixed with the same volume of quartz powdered charcoal to prevent caking, are placed in a ass tube 30 to 40 centimeters (11.8 to 15.74 inches) ng and 13 to 15 millimeters (0.51 to 0.59 inch) wide, osed at one end. The other end is introduced into other glass tube, also closed at one end, and the sub-ance is then heated in a combustion furnace (Fig. 58, 230), or by another source of heat (p. 62). The end the tube containing the sublimed sulphur is cut off and eighed. The sulphur is then volatilized by heat and e tube again weighed. Pure iron pyrites gives on a rge scale at the utmost 23 per cent. of sulphur ($7FeS_2 = 6FeS.FeS_2 + 6S$); copper pyrites not more than 9 r cent. ($Cu_2S + Fe_2S_3 = Cu_2S + 2FeS + S$).

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[1] Dingler, ccxxx. 66.

74. ASSAYS OF SULPHUR FOR THE DETERMINATION OF THE QUANTITY OF SULPHUR CONTAINED IN A SUBSTANCE.

These assays may be executed in order to determine the yield of an ore in sulphurous acid, for the manufacture of sulphuric acid, or its yield of sulphur for the formation of raw matt, for controlling roasting, etc. For this the wet method is more frequently used than the dry method.

A. Dry assay (raw matt assay).—The object of this assay is to determine the quantity of metallic sulphides, especially iron sulphide, contained in an ore, after the oxidized and earthy, etc. substances mixed with it have been separated by solvent agents.

A mixture of 5 grammes (77.16 grains) of ore and 0.5 gramme (7.71 grains) of resin is introduced into a crucible (Fig. 42, p. 67). Upon this is placed 10 to 15 grammes (154.32 to 231.48 grains) of borax, 5 to 10 grammes (77.16 to 154.32 grains) of glass free from heavy metals, a cover of common salt, and a fragment of coal. The charge is fused at a bright red heat in the muffle or wind furnace for 30 to 45 minutes after the "flaming" has ceased. The resulting button of iron sulphide which is brittle and oxidizes and disintegrates quickly, is carefully freed from slag which should be well fused. It is then weighed and broken up in order to recognize the presence of foreign metallic sulphides by the appearance of the fracture. When only iron pyrites are present, this has a fine grain and speiss yellow color; with copper pyrites, brass yellow; with lead and sulphide, grayish and foliated; with zinc blende, radiated or foliated, of a sub-metallic lustre, and blackish-gray; with metallic antimony and arsenic, a fine grain and light gray.

Hungary:[1] If the ores are easily fusible, 5 grammes (77.16 grains) are charged with a flux composed of 2 parts of calcined borax and 1 part of glass free from iron, by placing a mixture of ore and 11.5 grammes (177.47 grains) of flux in the bottom of the crucible, upon this 23 grammes (354.94 grains) of flux, and on the top 8 to 10 grammes (123.46 to 154.32 grains) of common salt. This is fused in the muffle furnace. When the ores are refractory, 1.25 grammes (19.29 grains) are fused with the same flux, and 3.2 grammes (49.4 grains) of a pure easily fusible concentrated pyrite ore, the percentage of matt contained in this being afterwards deducted; or, with 0.25 to 3.5 grammes (3.85 to 54.01 grains) of copper as a collecting agent.—*Pribram:* 5 grammes (77.16 grains) are mixed with ⅔ the quantity of a flux consisting of 10 grammes (154.32 grains) of borax, 2 grammes (30.87 grains) of glass, and 0.4 gramme (6.17 grains) of coal dust. The remaining ⅓ part of the flux is strewn over this, and on top a cover of common salt and fragment of coal. 0.05 gramme (0.77 grain) of copper may be added to the roasted, and as much as 0.2 gramme (3 grains) to unroasted ores. The crucible, with luted cover, is gradually heated to a moderate red heat in an anthracite furnace (p. 56), and then fused for from 30 to 35 minutes at a bright red heat.—*Slags* with mechanical inclosures of matt are charged in the following manner: 30 grammes (462.97 grains) of slag, 20 grammes (308.64 grains) of borax, and 50 grammes (771.61 grains) of glass with a covering of common salt and a fragment of coal. The charge is fused for ½ to ¾ of an hour at a bright red heat.

B. Wet assays.[2]

1. *Gravimetric assay.*—1 gramme (15.43 grains) of ore is decomposed by fuming nitric acid, then nearly all the nitric acid removed by boiling. Hydrochloric acid is now added and heat is applied, when the sulphur will be quickly dissolved (the heating should not be continued too long, or loss will ensue by the escape of sulphuric acid). The solution is then evaporated to dryness, the residue is heated with hydrochloric acid in order to expel the nitric acid (as otherwise the results would be too high). The liquid is now diluted

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[1] B. u. h. Ztg. 1871, p. 255.

[2] Muspratt's techn. Chem. vi. 8.

and filtered, the filtrate precipitated with barium chloride, and the barium sulphate filtered through impervious Swedish paper, dried, ignited, and weighed ($BaSO_4$, with 34.356 per cent. SO_3 and 13.73 per cent. S). The sulphur in *pyrites*, roasted pyritous ores, and the same *lixiviated*,[1] is determined by heating 0.5 gramme (7.71 grains) of the substance in a platinum crucible, together with 10 parts of a mixture of 2 parts of sodium carbonate and 1 part of saltpetre. This is lixiviated, etc., and finally precipitated by barium chloride, etc., as above.—Process for determining small quantities of *sulphur in materials* and *products of the iron-works* at *Creuzot*.[2] The substance is heated in a porcelain tube, and a mixture of $\frac{3}{4}$ of hydrogen and $\frac{1}{4}$ carbonic acid is conducted over it. The sulphuretted hydrogen, which is formed, is led into an acid silver solution, and the quantity of sulphur calculated from the weight of the silver sulphide.

2. *Volumetric assays.*[3]

a. 1 gramme (15.43 grains) of ore is intimately rubbed together with 2 grammes (30.87 grains) of pure saltpetre, or with 3 grammes (46.30 grains) of sodium carbonate and the same quantity of saltpetre. The mixture is placed in a small dish of sheet iron, 55 millimeters (2.16 inches) wide and 25 millimeters (0.98 inch) deep, which is placed in a scorifier (Fig. 37, p. 65). It is then gradually heated in a red-hot muffle. After fusing quietly from five to eight minutes, the small dish is taken out and allowed to cool off. The mass contained in it is then lixiviated with hot water and filtered into a small beaker-glass. The residue is washed out with as little water as possible, and hydrochloric acid in excess then gradually added. It is now heated in a sand-bath, in order to expel the nitrous compounds. Titrated solution of barium chloride is then added drop by drop to the hot solution (which has been concentrated as much as possible), from a burette, divided into ¼ cubic centimeter (0.015 cubic inch), until no further white turbidity is formed in the supernatant liquid. 1 cubic centimeter (0.061 cubic acid) of a normal solution, with 0.152 gramme (2.34 grains) of barium chloride, precipitates 0.050 gramme (0.77 grain) of sulphuric acid, corresponding to 0.020 gramme (0.3 grain) of sulphur; or 5 per cent. of sulphuric acid and 2 per cent. of sulphur. Some experience is required to detect the final reaction. Indicators for this have been proposed, as, for instance, potassium chromate, by *Wildenstein*, or filtering off a few drops and adding barium chloride.

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[1] Fresenius' Ztschr. 1877, p. 335. B. u. h. Ztg. 1877, p. 241.

[2] Dingler, ccxxxiii. 124 (Rollet).

[3] Muspratt's techn. Chem. vi. 9. Fresenius' Ztchr. i. 323 (Wildenstein).

According to *Wildenstein*, the solution containing sulphuric acid is diluted to a bulk of 45 to 55 cubic centimeters (2.74 to 3.35 cubic inches), to which is added a slight excess of titrated solution of barium chloride. It is then boiled for a half to one minute, a slight excess of ammonia free from carbonic acid having first been added. Titrated solution of neutral potassium chromate is now added in small quantities, which should not exceed ½ cubic centimeter (0.03 cubic inch) at a time, in order to precipitate the excess of barium monoxide, until the liquid, after having been shaken and allowed to become clear, shows a distinct yellow color. It is then titrated back with a few drops of barium chloride until the fluid becomes colorless. During this operation the precipitate must be allowed to settle every time, or a few drops should be filtered off, and tested. Normal solutions: 1 cubic centimeter (0.061 cubic inch) of barium chloride = 0.015 gramme (0.23 grain) of sulphuric acid, and 1 cubic centimeter (0.061 cubic inch) of solution of potassium chromate = 0.01 gramme (0.15 grain) of sulphuric acid. This assay gives accurate results to within ⅕ per cent. of sulphur.

b. Metallic sulphides decomposable by hydrochloric acid are treated with it in a flask connected with a retort

(Fig. 61', p. 253). The sulphuretted hydrogen developed is introduced into a titrated solution of iodine in potassium iodide ($SH_2 + I_2 = 2IH + S$), and the unchanged iodine titrated with sodium hyposulphite[1] (p. 254).

XIX. FUELS.

75. FUELS.[2]

These may be in either of the following forms: solid (raw or natural, carbonized, or artificial, agglomerated or patent fuel briquetts); or liquid (petroleum, tar-oils); and gaseous (natural gas, waste and generator gases, illuminating gas).

The different varieties of raw fuel are, approximately, composed as follows:—

	C	H	O
Woody fibre (cellulose = $C_6H_{10}O_5$)	44.44	6.17	49.39
Peat	60.44	5.96	33.60
Lignite	66.96	5.27	27.76
Earthy brown coal	74.20	5.89	19.90
Bituminous coal, recent	76.18	5.64	18.07
" " ancient	90.50	5.05	4.40
Anthracite coal, recent	92.85	3.46	3.19
" " ancient	94.20	2.50	3.30

In order to remove *earthy admixtures* from fossil fuel before subjecting it to docimastic test, it is comminuted and stirred into sulphuric acid of 1.4 specific gravity (in soda manufactories, in a solution of sodium sulphate[3]). The heavier earths will fall to the bottom, while the coal rising to the surface is removed with a spoon, thoroughly washed, and dried.

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[1] Dingler, ccx. p. 184.

[2] Kerl, Grundr. der allgemeinen Hüttenkunde, 2 Aufl., 1879, p. 64. Muck in B. u. h. Ztg. 1876, p. 286 (Steinkohlen).

[3] Dingler, cxc. 76.

76. ASSAYS OF FUEL.

The examination extends to the following points, on which the value of fuel chiefly depends:—

1. *Determination of the amount of hygroscopic water.* —5 grammes (77.16 grains) of the powdered sample are placed in a watch-glass and heated on a water-bath (raw fuel), or (wood-charcoal, coke) at a higher temperature (120° to 150° C., 248° to 302° F.) in an air-bath, or on a drying disk (Fig. 2, p. 26). It is allowed to become cold in the desiccator (Fig. 17*a*, p. 43), and then weighed; is again dried and weighed until two weighings agree.

Air-dried wood and peat contain 15 to 20 per cent. of water; lignite, 10 to 15 per cent.; brown coal with a conchoidal fracture, 10 to 5 per cent.; earthy coal, as much as 25 per cent.; bituminous and anthracite coal, fresh from the pit, 1 to 10 per cent.; wood-charcoal, 10 to 12 per cent.; coke, 5 to 10 per cent.

2. *Yield of carbon.*—5 to 10 grammes (77.16 to 154.32 grains) of the material, either in small fragments, or in the form of powder, are placed in a covered crucible (Fig. 42, p. 67), and gradually heated to a red heat in the muffle furnace, until the flame which shows itself at the lid of the crucible disappears. The residue, upon cooling, is weighed, and (in tests of coal) the physical condition of the coke is observed at the same time. This may be more accurately ascertained by heating 1 gramme (15.43 grains) of coal in a platinum crucible 40 millimeters (1.57 inches) high with a bottom diameter of 24 millimeters (0.94 inch), keeping the crucible at a distance of 3 centimeters (1.18 inches) over the flame of a gas-burner.[1]

The yield of carbon will vary according as the heat is raised more or less quickly, and with the degree of temperature, decreasing as the latter is more intense. Therefore, if several varieties of fuel are to be compared, the carbonization must be conducted at the same temperatures. The yield is generally less than that indicated by assay on the large scale. The average yield from wood charcoal in heaps is 21 to 22 per cent. by weight; from pine wood, 55 per cent., and from hard wood, 48 per cent. by volume; and respectively 25 to 27 and 60 to 65 per cent. in furnaces; from more recent bituminous coal as high as 60 per cent.; from semi-bituminous coal, 78 to 83 per cent.; from anthracite coal, 84 to 87 per cent., and from real anthracite, 88 to 93 per cent. by weight.

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[1] B. u. h. Ztg. 1876, p. 287.

Determination of the coking quality of coal according to *Richters*,[1] 1 gramme (15.43 grains) of coal in a finely powdered condition is mixed either with 0.1, 0.2, 0.3, etc., that is to say, as many times 0.1 gramme (1.54 grains) of powdered quartz as may be necessary to just crush the cake of coke remaining in the covered porcelain crucible after ignition, when weighed with a 0.5 kilogramme (1.1 lb.) weight carefully placed upon it. If 0.5 gramme (7.71 grains) of powdered quartz has been used, the coking quality of the coal would be represented by 5, etc.

3. *Volatile products* are determined from the difference in weight between the coke and raw fuel, after deducting the percentage of water. The amount of gas a coal will yield is ascertained by heating 5 grammes (77.16 grains) of the sample in a glass retort or tube. The gas evolved (after passing through two wash-bottles filled respectively with baryta water and lead acetate to absorb carbonic acid and sulphuretted hydrogen) is collected over mercury in a graduated cylinder (Fig. 58, p. 230).

4. *Determination of the ash.*—The residue from the assay for carbon (containing carbon and ash) is pulverized as fine as possible, placed in a roasting-dish (Fig. 7, p. 34)

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[1] Dingler, cxcv. 71.

and heated in the muffle, which should not be exposed to too strong a draught of air, until the black particles have entirely disappeared. The ash is then weighed, and its physical properties (color, whether caked or pulverulent, etc.) are at the same time examined.

Gypsum and iron pyrites undergo alteration during this operation, thus impairing the result of the assay. This must be especially taken into consideration when a contract for the purchase of coal is based upon the minimum amount of ash.[1]

Amount of ash in different kinds of fuel: Wood, 0.15 to 2 per cent., an average 1 per cent. (composed of about 70 per cent. of calcium carbonate and 20 per cent. of alkaline carbonates); wood charcoal, 3 to 4 per cent.; peat, 0.5 to 50, on an average from 6 to 12 per cent. (composed of, approximately, 35 per cent. of argillaceous sand, as much as 40 per cent. of magnesian gypsum, about 30 per cent. of ferric oxide, and 3 per cent. of alkalies, as well as some phosphoric acid and chlorine); brown coal, as high as 50 per cent., on an average from 5 to 15 per cent. (chiefly silicic acid, alumina, ferric oxide, lime, sulphuric acid, lesser quantities of magnesia, alkalies, chlorine, rich in sulphur in the form of gypsum and iron pyrites, poor in phosphorus); hard coals, 0.5 to 30 per cent.; the best coal, at an average from 4 to 7; medium quality 8 to 14; and poorer qualities over 14 per cent.—ash, mostly bisilicate of alumina with lime (1 to 20 per cent.), ferric oxide (1 to 75 per cent.), alkalies (0 to 3 per cent.), sulphur (0.5 to 2 per cent.). Coke, 1 to 30 per cent. (good coke about 10 per cent.), phosphorus 0.0025 to 0.05 per cent.—*The amount of sulphur*[2] *contained in a coal or its ash* is determined by fusing 1 gramme (15.43 grains) in a platinum crucible with 8 grammes (123.46 grains) of saltpetre, 4 grammes (61.73 grains) of potassium carbonate, and 16 grammes (246.92 grains) of common salt. The fused mass is lixiviated with water, hydrochloric acid is added, and the mass then filtered. The filtrate is precipitated with barium chloride, and the resulting barium sulphate containing 13.8 per cent. of sulphur is weighed (see also assays of sulphur).

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[1] B. u. h. Ztg. 1878, p. 61 (Muck).

[2] Schwefelbestimmung in Steinkohlen, etc. Oestr. Ztschr. f. Berg- u. Hüttenwesen, 1874, p. 11 (Eschka). Fresenius' Ztschr. xii. 82, 178; xiv. 16 (Sauer). B. u. h. Ztg. 1875, p. 228 (Hayes).

5. *Determination of heating power.*—In estimating the availability of a fuel for a given purpose, it is of the greatest importance to determine how much heat, equal parts by weight (*absolute heating effect*), or equal parts by volume (*specific heating effect*), of different fuels will produce. The intensity of the heat produced (*pyrometric heating effect*) may also be a point of investigation.

The latter may be determined by calculation or by the pyrometer,[1] either *Fischer's*[2] calorimeter or *Siemens'* electric pyrometer;[3] or by means of the fusing point of alloys by a modification of *Prinsep's* principle.[4] The specific heating effect is found by multiplying the absolute heating effect by the specific gravity of the fuel in question. *Berthier's* method of determining the absolute heating effect may be especially recommended for docimastic purposes.

Berthier's method of determining the absolute heating power is based upon *Welter's* law, according to which the absolute heating power of different combustible substances is proportional to the amounts of oxygen required for their complete combustion. The oxygen is taken from oxides (lead oxide), and the quantity of metal (lead) set free represents the quantity of liberated oxygen, and therefore the absolute heating power.

Welter's law is based upon the fact that, according to former experiments by *Rumford*, *Despretz*, and others, the absolute heating power of carbon to hydrogen is in the proportion of 1 : 3.03, and the respective amounts of oxygen required for the combustion of 1 part of these elements are in nearly the same proportion (1 : 3). But, according to recent investigations by *Favre*, *Silbermann*, and others, the absolute heating powers of carbon and hydrogen are, respectively, as 1 : 4.3; and, therefore, *Welter's* law has become obsolete, and the results obtained by *Berthier's* method are only approximate. They approach more closely to the truth, the richer in carbon and poorer in hydrogen the fuel is, while the results from combustible substances rich in hydrogen are from $\frac{1}{9}$ to $\frac{1}{2}$ too low compared with more accurate calorimetric determinations. His method is, nevertheless, frequently used in practice, it being very convenient and quickly executed, and under the above-mentioned conditions gives practically available results, especially in the examination of different varieties of the same kind of fuel.

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[1] Kerl, Grundr. der allg. Hüttenkunde, 1879, p. 85.

[2] Dingler, ccxxv. 468. Ber. d. deutsch. chem. Ges. 1879, p. 1694.

[3] Dingler, ccxvii. 291. B. u. h. Ztg. 1871, p. 450; 1873, p. 231, 396; 1874, p. 463; 1876, p. 156; 1877, p. 109.

[4] Freiberger Jahrb. 1879, p. 154. B. u. h. Ztg. 1879, p. 126 (see Appendix).

Exactly 1 gramme (15.43 grains) of the finely divided fuel is weighed out, and intimately mixed with 40 to 50 grammes (617.29 to 771.62 grains) of litharge finely sifted and free from globules of lead, organic substances, and minium; or, still better, with 70 to 90 grammes (1080.26 to 1388.91 grains) of white lead. The mixture is covered with 20 to 25 grammes (308.65 to 385.81 grains) of litharge (or, 30 to 40 grammes (462.97 to 617.29 grains) of white lead), a lid is placed upon the crucible, and the charge gradually heated in the muffle furnace (Fig. 25, p. 51) until it is completely fused. The heat is then increased for a short time, when the oxidizable constituents of the fuel will be consumed at the expense of lead oxide and will separate the more lead the richer they are in such constituents. After the charge has been fused, which requires from $\frac{1}{2}$ to $\frac{3}{4}$ of an hour, the crucible is taken out and allowed to cool off. The lead button is then freed from slag, brushed off, and weighed. The resulting weight is divided by the quantity of the sample used in order to learn how much lead has been reduced by it. The thermal value of *graphite*[1] may also be determined by this assay.

In the case of combustible materials *decomposable at a lower temperature*, *lead oxychloride*, which is more easily fusible, should be used. It is obtained by fusing 3 parts by weight of red litharge together with 1 part of lead chloride in a Hessian crucible. 1 gramme (15.43 grains) of the fuel is mixed with 40 grammes (617.29 grains) of the oxychloride, and the mixture covered with 30 grammes (462.97 grains) of the latter.

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[1] Kerl, Thonwaarenindustrie, 1879, p. 91.

1 part of pure carbon reduces 34 (more accurately 34.52) times the quantity of lead; wood, 12 to 15, on an average 13.95 parts (=3200 heat units = 0.41 per cent. carbon); peat 8 to 18, Irish varieties as much as 27 parts; brown coal 14 to 26 parts; bituminous coal 23 to 31 parts, and anthracite 26 to 33 parts; wood charcoal 28 to 33.7 parts; coke 22 to 30 parts of lead. If the fuel contains iron pyrites, the quantity of lead reduced increases (1 part FeS_2 reduces 8.72 parts, and 1 part FeS, 7.18 parts of lead from litharge). Suppose p to be the weight of the lead button, the heating power in calories or heat units is expressed by $x = \frac{8080}{34.5} p = 234\, p$. In case the fuel contains a large amount of hydrogen, this value must be multiplied with a coefficient lying between 1 and $\frac{9}{8}$.

Suppose 100 kilogrammes (220 pounds) of coal must be replaced by wood in some smelting process in a reverberatory furnace. How much of the latter must be taken? The absolute heating power of both must be determined according to *Berthier's* method, according to which they are capable of reducing, respectively, 24 and 14 parts of lead. Then $14 : 24 = 100 : x$ and $x = 170$ kilogrammes (374 pounds) of wood supply the place of 100 kilogrammes (220 pounds) of coal. If the quantities of fuel are to be determined by the *volume*, it is only necessary to multiply the above numbers, 24 and 14, by the specific gravity of the fuel in question, and to formulate the resulting products into a similar proportion.

6. *Physical and chemical behavior.*—The following points must be considered as exerting an influence upon the action of combustible substances in the fire, during transportation, etc.: structure, density (compactness), form and size of the lumps, specific gravity, behavior when thrown into the glowing muffle, or in the furnace (whether they kindle easily or difficultly, burn quietly or

fly into pieces, whether the flame is short or long, or more or less smoking, the liberation of odors, brittleness, etc.), chemical composition of the fuel, and of the pulverulent, sintered, or clinkered ash, etc.

77. EXAMINATION OF FURNACE GASES.

To be able to judge the processes taking place during combustion,[1] the velocity of the flue gases, and the amount of air passing through the furnace are determined by an *anemometer*,[2] the strength of the draught by a *draught meter*,[3] the intensity of the heat by a *pyrometer*,[4] and the amount of *carbonic acid*, *carbonic oxide*, and *free oxygen* in the furnace gases are ascertained—

1. By means of *Orsat's apparatus*.[5]—With some experience and intelligence this apparatus gives results available for practical purposes, even in unscientific hands. It is based upon the principle, that a measured volume of gas is conducted through agents for the absorption of its principal constituents (caustic potassa for carbonic acid, potassium pyrogallate for oxygen, and solution of cuprous chloride for carbonic oxide), the volume of gas remaining after each absorption being measured, when the amount

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[1] Kerl, Thonwaarenindustrie, 1879, p. 301.

[2] Töpfer- u. Ziegler-Ztg. 1878, No. 1.

[3] Dingler, clxxi. 43 (List). Notizbl. der deutsch. Ver. f. Fabrikation von Ziegeln u. s. w. ix. 96 ; xi. 191 ; xiii. 40, 42. Töpfer- u. Ziegler-Ztg. 1877, No. 46.

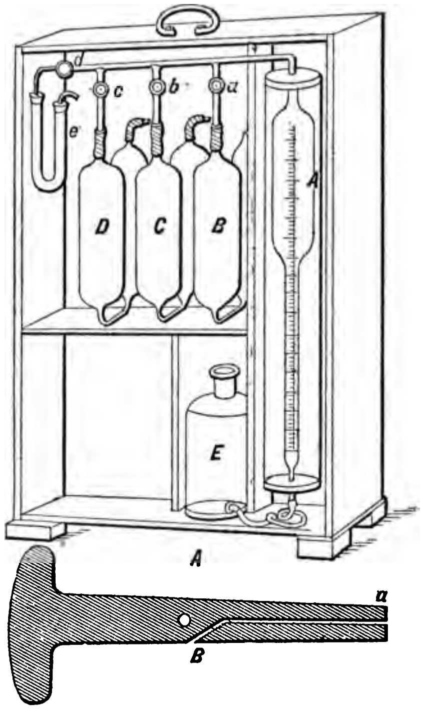
[4] Kerl, Grundr. d. allg. Hüttenkunde, 1879, p. 85. Mitchell, Practical Assaying, p. 131.

[5] Fichet-Ramdohr, Gasfeuerung, Halle, 1875. Ann. des mines, vol. viii. livr. 6 de 1875. B. u. h. Ztg. 1874, p. 232 ; 1875, p. 143 ; 1876, p. 72 ; 1877, p. 147. Dingler, ccxix. 420 (Weinhold). Fresenius' Ztschr. 1877, p. 343 (Seyberth). Oest. Ztschr. 1877, No. 11, 13, 16. Ztschr. de Ver. deutsch. Ing. xx. 318. Dingler, ccxxvii. 258 ; ccxxix. 262 (Fischer.) Winkler, Anleitung z. Chem. Untersuchung der Industriegase, 2 Abth., 1877, p. 1859.

of each will be ascertained from the difference. The apparatus is placed in a portable wooden case, and, according to *Fischer's* latest construction, is arranged as follows, (Fig. 63):—

A is a burette inclosed in a glass cylinder. Its lower end is connected with the water flask *E* by means of a rubber tube. The burette is capable of holding 100 cubic centimeters (6.1 cubic inches). Its lower part holding 40 cubic centimeters (2.44 cubic inches) is graduated to one-fifth cubic centimeter (0.012 cubic inch), and the upper part in whole cubic centimeters (0.061 cubic inch). *B C D* are the absorption vessels (*B* for caustic potassa, *C*

Figs. 63 and 64.



for potassium pyrogallate, and *D* for solution of cuprous chloride, or a fluid obtained by shaking copper hammer scale with a mixture of equal volumes of ammonia and cold saturated solution of sal ammoniac). The vessels are filled with fine glass tubes and connected with the burette by means of a system of thick-walled capillary tubes. *a b c* are plain cocks; *d* is a *Winkler* cock (Fig. 64, *B*), which besides having a simple perforation is also cut lengthwise. The outer end, *a*, is connected with an aspirator by means of a rubber tube. When the cock is properly set, the tube *e* (which is provided with a little water, and loosely filled with cotton, in order to saturate the gas with water vapor and to retain dust), and the gas-conducting tube connected with it, can then be filled with the gas to be examined.

The operation is conducted as follows: The cock *d* is set so that it communicates with the outer air. The flask *E*, filled with water, is raised so that *A* will become completely filled with water, the air escaping from *d*. *d* is then closed towards *A*. The cock *a* is now opened and the flask *E* lowered, whereby the absorption vessel *B* is filled with the absorbing liquid (potassium hydrate) to the mark immediately below the cock *a*, whereupon this is closed. *C* is filled in a similar manner with potassium pyrogallate, and *D* with a solution of cuprous chloride from vessels of equal size communicating with and placed behind them. The furnace gas to be examined is aspirated through the aspirator, and the connection between *e* and *A* is established by the cock *d*, after the burette *A* has been completely filled by raising the flask *E*. The latter is then lowered, when *A* will be become filled with the gas. *d* being properly set, the gas is allowed to escape by again raising *E*, in order to expel any small quantities of air which may still be contained in the capillary tubes.

After A has in this manner been filled with gas, this is successively forced by the same manipulation through B, C, and D, and each time returned to A, in order to measure the volume of gas which has been absorbed respectively in B, C, and D.

Orsat has further enlarged his apparatus so that hydrogen and carburetted hydrogen can be also determined.[1] An apparatus for examining gas, by *Schwackhöfer*,[2] has recently been recommended, it being claimed that it is less easily broken and safer to handle than *Orsat's*.

2. *By means of Bunte's burette*[3] (Fig. 65).—An unlimited number of absorbing agents can be used in this apparatus, as it allows of the removal of the absorbing liquids from the burette without a loss of gas every time after they have been used, and further permits the gas inclosed in the burette to be brought, after each absorption, to the same pressure. A is a burette divided from the *Winkler* cock, a, to the common cock, b, into some what more than 110 cubic centimeters (6.71 cubic inches) and fractions. t is a funnel forming the upper part of the burette, having a capacity of 25 cubic centimeters (1.52 cubic inches) to the mark m. The burette, A, is filled with gas by connecting a with the gas-conductor by means of a rubber tube, and aspirating the gas through b until all the air has been expelled from A. a and b are then closed, and a rubber tube, plugged at one end with a small glass rod, is pushed over the point of a. In order to bring the volume of gas in the burette to 100 cubic centimeters (6.1 cubic inches) under a known pressure,

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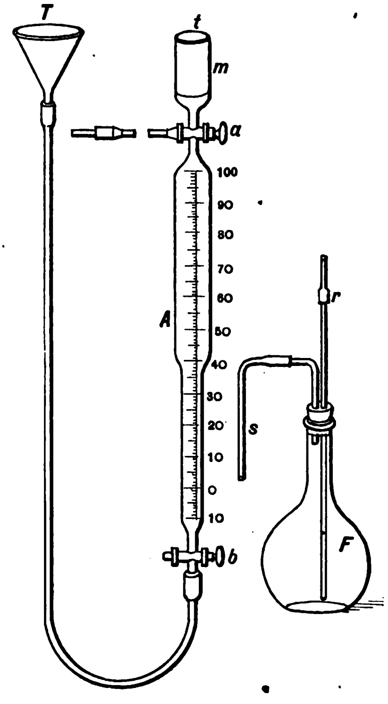
[1] Ann. d. min. 1875, t. viii. p. 501. Oest. Ztschr. 1877, No. 13. B. u. h. Ztg. 1878, 123. Dingler, ccxxi. 284; ccxxvii. 171 (Fischer). Winkler, Anl. z. chem. Untersuchung der Industriegase, 2 Thl. p. 198.

[2] Ztschr. der berg- u. hüttenm. Ver. für Steyermark u. Kärnthen, 1878, No. 3–6, p. 78.

[3] Dingler, ccxxvii. 167; ccxxviii. 46.

er is forced into the burette up to the 0 point by ns of a rubber hose filled completely with water, and iected with the funnel, *T*, and the point of the burette. then closed, and *a* opened towards *m*, whereby a part ie gas escapes, and the inclosed remaining part stands er the pressure of the atmosphere and a column of er a few cubic centimeters high. The gas can in a lar manner be brought under equal conditions of sure at any desired position of the liquid in the ette, and a correction the pressure, which is le the same at every ling, is not required in customary statement of results of the experi- its in per cents. of the l volume.

Fig. 65.



'he following is the pro- of manipulating when iace gases in the burette ;ain carbonic acid, car- ic oxide, and oxygen. minutely perforated it, *b*, of the burette is iected with the flask, by the rubber tube *r*. cock *b* is then open- and air drawn out ugh the tube *s* by ion, whereby water is vn from the burette *A* to *F*, and then *b* is imme- ely closed. The flask, *F*, is removed from the burette, the point of this is dipped into a dish containing tion of potassium hydrate. When the cock *b* is

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opened, this enters *A*, and replaces the water drawn out. The burette is held by its extremities and gently shaken for the absorption of the carbonic acid. As soon as this has been accomplished, *t* is connected with *A*, by the cock *a*, whereby water enters into *A*, until the pressure is completely equalized. The volume of *carbonic acid*, which has disappeared, is read off on the burette. The *oxygen* is determined in a similar manner by withdrawing a part of the potassium hydrate by suction, and allowing potassium pyrogallate to enter; while for the determination of the *carbonic oxide*, the potassium pyrogallate must be entirely removed from the burette by repeatedly aspirating the liquid from *A*, through *b*, and allowing water to flow in through *a* from *t*, until the absorbing agent has been entirely removed, when solution of cuprous chloride is introduced in the manner indicated.

APPENDIX.

A. TABULAR SYNOPSES.

1. *Atomic Weights.*

	Old equivalent weights.	New atomic weights.		Old equivalent weights.	New atomic weights.
inium	13.7	27.4	Mercury	100	200
nony	122	122	Molybdenum	46	96
ic	75	75	Nickel	29.3	58.6
m	68.5	137	Niobium	47	94
lium	4.7	9.3	Nitrogen	14	14
uth	210	210	Osmium	99.2	199.4
n	11	11	Oxygen	8	16
ine	80	80	Palladium	53.3	106.6
ium	56	112	Phosphorus	31	31
m	133	133	Platinum	99	198
um	20	40	Potassium	39	39.1
n	6	12	Rhodium	52.2	104.4
m	....	91.2	Rubidium	85.5	85.5
ine	35.5	35.5	Ruthenium	52.2	104.4
nium	26.1	52.2	Selenium	39.7	79.4
t	29.5	59	Silicium	14	28
er	31.7	63.4	Silver	108	108
nium	48	95	Sodium	23	23
m	56.3	112.6	Strontium	43.8	87.6
ine	19	19	Sulphur	16	32
m	....	68.8	Tantalum	91	182
	197	197	Tellurium	64	128
ogen	1	1	Thallium	204	204
m	56.7	113.4	Thorium	....	232.4
e	127	127	Tin	59	118
m	99	198	Titanium	25	50
	28	56	Uranium	60	120
anum	46	93	Vanadium	....	51.3
	103.5	207	Wolfram	92	184
m	7	7	Yttrium	30.85	61.7
esium	12	24	Zinc	32.6	65.2
anese	27.5	55	Zirconium	44.8	89.6

2. *Fusing Points of Metals and Furnace Products,*[1] *Glowing Temperatures.*

	Fusing point (Celsius).	Fusing point (Fahr.).	Glowing temper'ture (Celsius).	Glowing temper'ture (Fahr.).
Tin	228°	442.4°		
Bismuth	264	507.2		
Thallium	290	554		
Cadmium (455° C., 851° F.) (boiling point 891° C., 1635.8° F.) .	320	608		
Lead	335	635		
Zinc (boiling point according to Becquerell 891° C., 1635.8° F., according to Deville 1040° C., 1904° F.)	412	773.6		
Antimony	432	809.6		
Incipient redness . . .	....	....	525°	977°
Dark redness . . .	....	....	700	1292
Aluminium	700	1292		
Incipient cherry-redness .	....	....	800	1472
Strong cherry-redness . .	....	....	900	1652
Bronze	900	1652		
Litharge	954	1749.2		
Complete cherry-redness .	....	....	1000	1832
Silver (according to Becquerell 916° C., 1680.8° F.) . .	1000	1832		
Copper matt	1002	1835.6		
Brass	1015	1859		
Lead matt	1027	1880.6		
Black copper	1027	1880.6		
Raw matt	1047	1916.6		
Lead speiss	1062	1943.6		
Copper	1090	1994		
Gold (according to Becquerell 1037° C., 1898.6° F.) . .	1200	2192		
Bright redness . . .	....	....	1200	2192
White heat	....	....	1300	2372
Lead and lead matt slag . .	1315-1330	2399-2426		
Raw slag	1330-1360	2426-2480		
Black copper slag . . .	1345	2453		
Blast furnace slag . . .	1390-1430	2534-2606		
Cobalt (1400° C., 2552° F.).				
Strong white heat . .	....	....	1400	2552
Dazzling white heat . .	....	....	1500-1600	2732-2912
Cast iron (according to Becquerell 1050 to 1200° C., 1922 to 2192° F.)	1500-1700	2732-3092		
White crystalline pig iron according to v. Tunner . . .	1600	2912		
Gray charcoal pig iron according to v. Tunner	1700	3092		

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[1] The older fusing points mostly according to Plattner ; those inclosed in brackets are newer, according to Becquerell.

	Fusing point (Celsius).	Fusing point (Fahr.).	Glowing temper'ture (Celsius).	Glowing temper'ture (Fahr).
Palladium (according to Becquerell 1360 to 1380° C., 2480 to 2516° F.)	1600°	2912°		
Nickel (1600° C., 2912° F.) .				
Wolfram (1700° C., 3092° F.) . .				
Manganese (according to John 1500° C., 2732° F., according to Becquerell 1600° C., 2912° F.)				
Uranium and molybdenum (1600° C., 2912° F.) . .				
Chromium (1700° C., 3092° F.)				
Steel (according to Becquerell 1300 to 1400° C., according to v. Tunner 1850° C., 3362° F.)	1700–1900	3092–3452		
Malleable iron (according to Becquerell 1600° C., 2912° F.) .	1900–2100	3452–3812		
Platinum (according to Debray 2000° C., 3632° F., according to Becquerell 1460 to 1480° C., 2660 to 2696° F.) . . .	2534	4593.2		
Iridium (2400° C., 4352° F.) .				

Plattner's method is based upon Prinsep's principle (determination of temperatures by the fusing points of alloys), but his deductions are untenable, although probably approximate for the average of commencing fusion of substances. The determination of the fusing point of the old furnace products of the Freiberg smelting works is also of but little importance at the present time, as these products have lately been materially changed by new processes.

Erhard and Schèrtel have recently made experiments with the aid of their improved pyrometer to determine the fusing points of metals, alloys, furnace products, silicates, minerals, and rocks. As these may be considered at the present as the most reliable, we give them in the following table.

3. *Fusing Points of Metals, Alloys, Furnace Products, Rocks, and Silicates, according to Erhard and Schertel.*[1]

a. Metals and Alloys.

		Degrees Celsius.	Degrees Fahrenheit.
Ag		954	1749.2
80 Ag	20 Au	975	1787
60 "	40 "	995	1823
40 "	60 "	1020	1868
20 "	80 "	1045	1913
Au		1075	1967
95 Au	5 Pt	1100	2012
90 "	10 "	1130	2066
85 "	15 "	1160	2120
80 "	20 "	1190	2174
75 "	25 "	1220	2228
70 "	30 "	1255	2291
65 "	35 "	1285	2345
60 "	40 "	1320	2408
55 "	45 "	1350	2462
50 "	50 "	1385	2525
45 "	55 "	1420	2588
40 "	60 "	1460	2660
35 "	65 "	1495	2723
30 "	70 "	1535	2795
25 "	75 "	1570	2858
20 "	80 "	1610	2930
15 "	85 "	1650	3002
10 "	90 "	1690	3074
5 "	95 "	1730	3146
Pt		1775	3227

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[1] Freiberger Jahrb. 1879, p. 154. B. u. h. Ztg. 1879, p. 126.

b. Furnace Products and Gangues.

	Corresponding alloy.	Temperature degrees Celsius.	Temperature degrees Fahrenheit.
Slag from working the ores in the Muldner smelting works (porous) The same rich in zinc (porous) . .	70 Au 30 Ag	1030	1886
The same two slags entirely fused .	90 Au 10 Pt	1130	2066
Concentration slag of copper matt .	80 " 20 Ag	1045	1913
Melaphyre from Mulatto . . . . Pitchstone from Arran	94 " 6 Pt	1106	2022.8
Asbestos	60 " 40 "	1300	2372
Temperature in the porcelain kiln	50 " 50 "	1400	2552
Blast furnace slag ($50SiO_2$, $17Al_2O_3$, 3FeO, 30CaO) . . . . Fusing point 77Au 23Pt=1208°C. (2206.4° F.).	49 " 51 "	1392 formation temp.	2537.6
Freiberg raw slag ($48SiO_2$, $9Al_2O_3$, 37FeO, 4.5CaO, 1.5MgO) . . .	59 " 41 "	1326	2418.8
Freiberg lead slag ($36.5SiO_2$, 40.5FeO, $8.5Al_2O_3$, 4CaO, 3MgO, 7.5BaO) Fusing point 85Au 15Pt=1160° C. (2120° F.).	75 " 25 "	1220	2228
Freiberg black copper slag ($32.7SiO_2$, 60.3FeO, $7Al_2O_3$) . . . . Fusing point 83Au 17Pt=1172° C. (2141.6° F.).	67 " 33 "	1273	2323.4
Raw slag from 3.45 dry ore and 5.25 lead slag . . . . 2.4 raw matt, fusing point 83Au 17Pt=1172° C. (2141.6° F.).	68 " 32 "	1267	2312.6
Lead slag from 2.34 roasted lead ore, 1.80 roasted raw matt, 5.00 lead slag, 0.30 powdered coke .	77 " 23 "	1208	2206.4

B. LOWER HARZ WORKING ASSAYS.

According to *Bräuning*[1] the following methods are used in the *Oker* assay laboratory for assaying the *Rammelsberg* ores and the furnace products obtained from them, after 25,000 to 75,000 kilogrammes (55,000 to 165,000 lb.) have been broken into pieces the size of a fist. A few grammes of samples are taken by crossing; these are comminuted in a stamping-mill, powdered fine in a mortar, and sifted.

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[1] Zeitschr. f. Berg-, Hütten-, u. Salinenwesen im Preuss. Staate, Bd. 25.

a. Lead (p. 94).—3.75 to 7.5 grammes (57.87 to 115.74 grains) of the ore are decomposed with *aqua regia* and evaporated with addition of sulphuric acid. The mass is then digested with diluted sulphuric acid, and filtered. The filtrate is placed on the roasting-dish and dried under the muffle. The mass is then mixed with three times the quantity of black flux (1 part of saltpetre and 2 parts of argol), and placed in a crucible (Fig. 39, p. 66). 0.75 to 1.13 grammes (11.57 to 17.44 grains) of iron wire and a thin covering of common salt are added, and the charge is fused under the muffle for from fifteen to twenty minutes.

b. Copper.—The filtrate from the test with sulphuric acid (a) is diluted to the bulk of 1 liter (1.76 pints). 250 cubic centimeters (15.25 cubic inches) of this are taken and treated with 10 to 15 cubic centimeters (0.61 to 0.91 cubic inch) of nitric acid of 1.2 specific gravity. The solution is then precipitated by sulphuretted hydrogen, and the precipitate, in case its color indicates the presence of considerable quantities of antimony and arsenic, is treated with sodium sulphide. The residue of copper sulphide is dissolved in 20 to 30 cubic centimeters (1.22 to 1.83 cubic inches) of moderately diluted nitric acid. This is diluted with water, filtered, and the copper precipitated by electrolysis (p. 115).—*Swedish assay* for the determination of copper in intermediate products. The object is attained more quickly by this method, but it is done at the expense of accuracy. 3.75 grammes (57.87 grains) of the assay sample are decomposed with *aqua regia*, and evaporated to dryness with sulphuric acid. The dry mass is then taken up with some diluted sulphuric acid, filtered, and the copper precipitated with zinc. The precipitated copper is then ignited under the muffle.—*Heine's colorimetric assay* (p. 128) for products poor in copper (slags, lixiviation residues). 3.75 grammes (57.87 grains) of the substance are decomposed by means of *aqua regia.* The solution is supersaturated with ammonia and filtered. It is then diluted to a known volume and compared with standard solutions.

c. Iron.—The filtrate from the precipitation with sulphuretted hydrogen (b) is oxidized with nitric acid. It is then evaporated to a small volume, and precipitated with ammonia. The precipitate is dissolved in hydrochloric acid, reduced with stannous chloride, and the excess of stannous chloride is titrated back with solution of iodine (*Kerl's Eisenprobirkunst*, 1875, p. 16).

d. Zinc (p. 212).—The filtrate from the iron precipitate is slightly acidulated with hydrochloric acid, and then tested for zinc with potassium ferrocyanide by the volumetric method.

e. Silver.—3.75 grammes (57.87 grains) of ore, etc., are placed in a scorifier with a mixture of 37.5 grammes (578.70 grains) of granulated lead and 0.55 to 0.75 grammes (8.49 to 11.57 grains) of borax, and with a cover of 0.37 gramme (5.71 grains) of borax, and the charge fused. The lead buttons are cupelled in cupels made of 3 parts of wood-ash and 1 part bone-meal. The buttons of silver are weighed.—*Black copper* and *crude copper* are fused with twenty times the quantity of granulated lead. The assay of fine silver is executed according to *Volhard's* method, it being simpler and more expeditious than that of *Gay-Lussac*, and equals the last-named in accuracy.

f. Gold.—The buttons obtained from fusing with lead (see *e*) are dissolved in nitric acid (free from chlorine) of 1.2 specific gravity. The solution is carefully heated to the boiling-point, and, when the action of the acid can no longer be perceived, the argentiferous solution is separated from the gold. The latter is carefully washed, placed in a tared porcelain crucible, gently ignited, and then weighed. In fine silver assays the percentage of gold is determined in the manner indicated on p. 157.

g. *Sulphur* (p. 259).—1.87 grammes (28.86 grains) of raw or roasted ore are digested for several hours, in the cold, with concentrated fuming nitric acid. An equal quantity of concentrated hydrochloric acid is added, and the liquid heated on the sand-bath, until the nitric acid has been driven off. It is then diluted with water, filtered, and the sulphuric acid precipitated with barium chloride. Or, by another method, which is more easily executed and gives sufficiently accurate results, the ore is fused with alkaline nitrates and carbonates in iron dishes under the muffle, etc. (p. 260).

C. SCHAFFNER'S ASSAY OF ZINC (P. 207) AS MODIFIED BY BRUNNLECHNER.[1]

Crystals of sodium sulphide are dissolved in water with the application of heat until the solution is supersaturated. The solution is then allowed to cool off and settle. The clear solution is poured off and diluted with 10 to 11 times the quantity by volume of water. It is then poured into a flask having the capacity of 4 to 5 liters (7.04 to 8.8 pints) and provided with a doubly perforated cork. Into one of them is fitted a glass siphon with a rubber tube and pinch-cock, and into the other a short, small, glass tube which may be closed by a cock or cork. The contents of the flask is thoroughly shaken, and, the flask being closed, the siphon is filled by blowing into the small tube and opening the pinch-cock at the same time. The liquid is then allowed to stand for at least twelve hours before it is used. Its strength will be diminished within twenty-four hours, to the extent of 2.5 to 3-thousandths by the oxidation of the sodium sulphide. As much chemically pure zinc as is approximately contained in the sample ore is then weighed off. If, for instance, the ore contains 40 per cent. and 0.5 gramme (7.71 grains) have been weighed off for the assay, about 0.2 gramme (3.08 grains) of pure zinc will be required. This is placed in a flask capable of holding half a liter (0.88 pint) and dissolved in 10 cubic centimeters (0.61 cubic inch) of concentrated hydrochloric acid. The solution is diluted with 100 cubic centimeters (6.1 cubic inches) of water, and treated with 50 cubic centimeters (3.05 cubic inches) of ammonia. It is then thoroughly shaken and allowed to stand for some time, as, otherwise, the indicator would be affected too quickly and the titer of the standard solution would be too high. 1 cubic centimeter of the solution should precipitate at least 8, and at the utmost, 10 milligrammes (0.12 and 0.15 grain) of zinc from the assay.

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[1] Oesterr. Zeitschr. f. Berg- u. Hüttenwesen, 1879, No. 37.

When the ore contains over 20 per cent. 0.5 gramme (7.71 grains), and, if less, 1 gramme (15.43 grains) of zinc carbonate and roasted zinc blende is dissolved in concentrated hydrochloric acid, to which a few drops of nitric acid have been added, but raw zinc blende and calamine are dissolved in *aqua regia.* In case gelatinous (ferruginous) silica should be separated, the solution should be diluted, the liquid poured off from the residue, the sediment on the bottom detached by means of a glass rod, again heated with acid, and the two liquids then united. In case sulphur should be separated from silicious zinc ores, fuming nitric acid or potassium chlorate is added. The solution is then evaporated to the consistency of syrup, in order to remove the excess of acid. The residue is then moistened with a few drops of hydrochloric acid and diluted with 20 cubic centimeters (1.22 cubic inches) of water. To this are added 30 cubic centimeters (1.83 cubic inches) of ammonia and 15 cubic centimeters (0.91 cubic inch) of ammonium carbonate. The solution is allowed to settle and then filtered into a flask of 500 cubic centimeters (30.51 cubic inches) capacity. The filter is washed with 30 cubic centimeters (1.83 cubic inches) of warm ammonia, and finally with warm ammoniacal water. When much ferric hydrate is present the precipitate is again dissolved and precipitated with ammonia and ammonium carbonate.—*Plumbiferous ores:* The assay sample is dissolved in nitric acid, and the solution evaporated with sulphuric acid. The lead and calcium sulphates are then filtered off. If the ore contains but little calcium, it may be treated with nitric acid, and the lead precipitated with 30 cubic centimeters (1.83 cubic inches) of ammonia, and 15 cubic centimeters (0.91 cubic inch) of sodium phosphate. When much calcium is present, the precipitate is again dissolved and precipitated.

A stand with three shelves is used. The uppermost shelf serves for the reception of the flask containing the sodium sulphide, the second smaller one, for a small flask with a pipette containing the indicator solution, and upon the lowest shelf, which projects somewhat, the flask containing the solution of zinc is placed. Over this, hangs a burette with a pinch-cock fastened to arms on the vertical wall, its mouth being directly under the orifice of the pinch-cock on the flask containing the standard solution. Duplicate titrations are then made, between which only decimal differences are allowable. Suppose E is the weight of the assay sample in cg., Q the quantity of standard solution in c. cm. used for the precipitation, [illegible] the total quantity of the assay solution in c. cm.; the titer will be—

$$T = \frac{100\,E}{[Q - (M \times 0.007)]}$$

if hydrated peroxide of iron has been used as the indicator, or

$$T = \frac{100\,E}{[Q - (M \times 0.005)]}$$

if paper saturated with ferric chloride (p. 209) has been used.

In titrating the samples, one-third to one-half of the approximate quantity of the precipitating agent required should be added every time to the solution and this well shaken. A drop of solution of ferric chloride is added to the zinc solution from a small pipette. The mass of hydrated peroxide of iron which is formed is broken up into as equally sized flakes of 1 to 1.5 millimeters diameter (0.039 to 0.059 inch) as possible by vigorously swinging the flask to and fro. This swinging is constantly continued while solution of sodium sulphide is added by cubic centimeters, until the color of the flakes commences to change. A minute is then allowed for the reaction of the particles of liquid which have remained ineffective, and the precipitation is then finished by adding sodium sulphide drop by drop. If V is the quantity of the precipitating agent consumed in c.cm., T the titer, M the total quantity of the solution in c.cm. after the assay is finished, the percentage of zinc when ferric hydrate has been used as indicator, will be—

$$Z = \frac{T}{100}\,[V - (M \times 0.007)]$$

and

$$Z = \frac{T}{100}\,[V - (M \times 0.005)]$$

when slips of paper saturated with ferric chloride have been used. When the first plan is employed the titration must be continued, in order to ascertain the titer, until the flakes become entirely black, but, in titrating solutions of ore, only until the reddish-brown color has passed into a greenish tint. The following conditions are required for obtaining a sharp reaction: the flakes must be nearly of the same size, the flask should be carefully swung to and fro to prevent the flakes from being broken up any further; not too much of the precipitating agent must be added at one time, and it should not fall directly upon the flakes, but run down the sides of the flask; the titration should be done at the ordinary temperature, whereby the reaction appears more gradually and uniformly, but the precaution must at the same time be observed of adding the standard solution at longer intervals; uniformity of quantity and time in treating the assays; judging the tone of color by reflected light; and finally the flake reaction should be controlled by a drop test.

If it is required to determine the amount of over 0.5 per cent. of lead in zinc ore, 2 grammes (30.87 grains of the sample are dissolved in nitric acid and evaporated to dryness. Some diluted sulphuric acid is added to the dry mass, and this is again evaporated until white vapors appear. It is allowed to become cold, diluted with 20 cubic centimeters (1.22 cubic inches) of water, filtered, and washed until the wash water shows no reaction with ammonium sulphide. The precipitate (lead sulphate, calcium sulphate, gangue) is rinsed off into a beaker and digested with a mixture of ammonium tartrate and ammonia in excess. The lead solution is filtered off, the lead precipitated with sulphuric acid, and the lead sulphate dried and weighed; or, it is detached from the filter, the latter incinerated, and the precipitate ignited (see also p. 98).

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